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Dissolution rates of mineral nitrogen fertilisers – Effects of moisture and precipitation

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Abstract

Hygroscopicity and deliquescence refer to the ability of a solid to absorb air moisture in which it dissolves and have long been recognised as properties having negative impacts on the product quality of explosives, pharmaceuticals, and fertilisers. Contrastingly, this thesis reconsiders and reappraises the hygroscopic effects of common mineral fertilisers, proposing hygroscopicity to beneficially enable quick dissolution under humid air conditions in absence of precipitation. Although precision fertilisation has improved, little is known about the dissolution dynamics of mineral nitrogen fertilisers in the field when exposed to either moist air or precipitation. In this thesis, dissolution rates of fertilisers based on ammonium nitrate (Axan™) and calcium nitrate (Kalksalpeter™), and of comparable pure salts, were recorded in a hygroscopicity test (≥90 % relative humidity at 25°C). Furthermore, dissolution rates of the fertilisers were also studied in a rain simulation (moderate intensity). In the hygroscopicity test, the pure reference salts had a higher hygroscopicity and shorter dissolution time relative the fertiliser products. The ammonium nitrate-based fertiliser and the pure ammonium nitrate salt moreover had higher dissolution rates (completely dissolved after 5.0 and 2.3 hours) compared to the corresponding calcium nitrate fertiliser and salt (21.1 and 4.3 hours respectively). All compounds tested dissolved within 24 hours. Endothermic properties, i.e. heat uptake during dissolution, seemed strongly correlated to the hygroscopic rates recorded. According to a thermodynamic calculation made, strongly endothermic salts had higher hygroscopicity compared to those with moderate or weak endothermic properties. In the rain simulation, the ammonium nitrate and calcium nitrate-based fertilisers required 5 and 6.5 mm of simulated precipitation, respectively. However, a theoretic estimation suggested less water to be sufficient at optimal application. For highly soluble fertilisers, the time during which the fertiliser is exposed to water may be more important from a dissolution point of view than the solubility. Considering the dissolution rates of fertilisers reported in this work, regardless if driven by hygroscopicity or precipitation, the limiting factor in the fertilisation system does not seem to be the dissolution but the dilution to concentrations non-toxic for crops. Future research should focus on the transport of dissolved nitrogen in the soil, at different soil moisture levels. Thereby, the time for a dry solid fertiliser to dissolve and reach the root zone of a crop could be better predicted.

Keywords: Hygroscopicity, Deliquescence, Fertilisers, Calcium Nitrate, Ammonium Nitrate, Dissolution rates, Rain simulation, Enthalpy, Precision fertilisation

Sammanfattning

Ett ämnes hygroskopicitet och delikvescens är dess förmåga att absorbera fukt ur luften och lösa sig i denna, en egenskap som i regel förknippas med kvalitetsförsämringar hos sprängmedel, läkemedel och mineralgödselprodukter. Under nederbördsfattiga förhållanden med tillräcklig luftfuktighet kan hygroskopiska egenskaper hos ett gödselmedel ändå vara mycket fördelaktiga och medge en snabb upplösning, även vid avsaknad av regn. Även om precisionsgödsling utvecklats på senare tid saknas fortfarande kunskap kring gödselmedlens upplösning i fält vid exponering för fuktig luft eller nederbörd. I denna uppsats har upplösningshastigheter bestämts för mineralgödselmedel baserade på ammoniumnitrat (Axan™) och kalciumnitrat (Kalksalpeter™) samt två rena referenssalter i en hygroskopimätning (≥90 % relativ luftfuktighet vid 25°C). Upplösningshastigheter för gödselmedel har vidare studerats i en regnsimulering med måttlig intensitet. I hygroskopitestet hade de rena referenssalterna högre hygroskopicitet och kortare upplösningstid än gödselprodukterna. Vidare hade det ammoniumnitratbaserade gödselmedlet och det rena ammoniumnitratsaltet högre upplösningshastighet jämfört med motsvarande kalciumnitratbaserade produkt och salt. Samtliga gödselmedel och salter löstes upp genom hygroskopi inom 24 timmar under ovan givna förutsättningar. Resultaten indikerar vidare att endoterma egenskaper, dvs. upptag av värme under upplösningsfasen, är en viktig faktor kopplad till uppmätta hygroskopiciteter. En termodynamisk beräkning visar att starkt endoterma salter verkar ha högre hygroskopicitet än svagt till måttligt endoterma salter. I regnsimuleringen krävde den ammoniumnitratbaserade gödselprodukten 5 mm simulerad nederbörd och den kalciumnitratbaserade 6,5 mm. Trots det visade en teoretisk uppskattning att långt mindre nederbörd skulle kunna vara tillräckligt för upplösning vid optimal applicering. För gödselmedel med hög löslighet skulle tiden under vilken de exponeras för vatten kunna vara mer väsentlig i upplösningssynpunkt än själva lösligheten. Oavsett om upplösningen drivs av hygroskopicitet eller nederbörd tycks den begränsande faktorn i tillförseln av näring till grödan ej vara upplösningsfasen utan huruvida tillräcklig utspädning kan erhållas för att undvika toxiska koncentrationer. En uppföljande modell över transport och utspädning i markprofilen skulle behövas för att kunna uppskatta tiden från applicering av gödselmedlet på markytan till upptag i rotzonen.

Nyckelord: Hygroskopi, Delikvescens, Gödselmedel, Kalciumnitrat, Ammoniumnitrat, Upplösningshastigheter, Regnsimulering, Entalpi, Precisionsgödsling

Populärvetenskaplig sammanfattning

Varje år sprids ansenliga mängder mineralkvävegödsel på åkermark världen över. Vid sidan av att öka skördarna kan användning av mineralkväve, likt annan kvävegödsling, även innebära en miljöbelastning. För att optimera användningen har precisionsgödsling utvecklats där mängd tillförd näring anpassas efter grödans behov. För att göra precisionen rättvisa bör vi dock även känna till under vilka omständigheter och hur snabbt gödselmedlet löser upp sig. Här saknas tillräcklig kunskap men litteraturen säger att vid sidan av nederbörd kan även fuktig luft lösa upp gödseln i en process benämnd hygroskopi. Syftet med denna uppsats var förutom att förstå upplösningsmekanismerna, också att mäta och kvantifiera upplösningshastigheterna av två vanliga kvävegödselmedel innehållande ammoniumnitrat (Axan™) respektive kalciumnitrat (Kalksalpeter™) som utsatts för antingen fuktig luft eller simulerad nederbörd. Då gödselmedel i regel är behandlade på ytan för att minska deras initiala vattenlöslighet testades också två rena referenskemikalier i hygroskopiförsöket för att utreda huruvida några skillnader i upplösning skulle kunna föreligga. I hygroskopiförsöket löstes gödselkornen upp i ett rum med över 90 % relativ luftfuktighet vid 25°C för att erhålla den snabbast potentiella upplösningstiden vid normal rumstemperatur. Regnsimuleringen å andra sidan utfördes i en regnsimulator, särskilt byggd för experimentet i vilken gödselkornen regelbundet sprayades med en bestämd mängd vatten motsvarande måttlig intensitet. Resultatet av mätningarna visade att samtliga testade gödselmedel och salter kunde lösa upp sig inom 24 timmar, i tre av fallen redan inom fem timmar, endast med hjälp av mycket fuktig luft. De rena referenskemikalierna utan ytbehandling hade en generellt sett snabbare upplösning. I regnsimuleringen krävdes 5 mm regn för att lösa upp Axan™ och 6,5 mm regn för Kalksalpeter™. En teoretisk uppskattning av nederbördsbehovet för fullständig upplösning, förutsatt att all nederbörd appliceras optimalt och kvarstår under hela upplösningsfasen, visade att det finns potential att lösa upp gödselkorn även med mindre nederbördsmängder. Det kräver dock att exponeringstiden för vatten och fukt är tillräckligt lång. Ur ett gödslingsperspektiv är den generella slutsatsen av mätningarna att upplösningen inte torde vara den begränsande faktorn utan snarare möjligheten till utspädning och transport från markytan till rotzonen. Koncentrationerna efter upplösning, antingen genom hygroskopi eller 5 – 6 mm nederbörd, är fortfarande för höga och rent toxiska om ingen utspädning sker. Om detta utspädnings- och transportsteg vidare kan utredas och modelleras skulle näringsförsörjningen av åkergrödan ytterligare kunna preciseras i tid och rum.

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Definitions

Caking	The tendency of a powder to form lumps
CAN	Calcium Ammonium Nitrate, a double-salt with the formula $5Ca(NO_3)_2*NH_4NO_3*10H_2O$
Coating	Conditioning agent protecting a solid against moisture and caking
Electrical conductivity	The ability of a solid or solution to conduct electricity
Deliquescence	Dissolution or melting by the sorption of gaseous water
Enthalpy of solution	Heat uptake or release during the dissolution of a substance
Granulation	Solidification of a chemical powder into granules
Hydrate	Inorganic salt containing water of crystallisation
Hygroscopicity	Absorption of gaseous water to a liquid solution
Prilling	Solidification method where a melt crystallises while cooling
Relative humidity	The concentration of water vapour in the air, at a certain temperature, relative the highest concentration possible at saturation
Vapour pressure	At equilibrium, the pressure a vapour exerts above the surface of its condensed phase.

1 Introduction

1.1 Nitrogen fertilisers and their solubility

Calcium nitrate ($Ca(NO_3)_2$) and ammonium nitrate (NH_4NO_3) are two highly hygroscopic and deliquescent inorganic salts, commonly used in mineral nitrogen fertiliser manufacturing. Their hygroscopic properties make the fertiliser salts sensitive to moisture and subsequently affect their drillability, storability and technical longevity (Adams & Merz, 1929). The term *hygroscopicity* refers to a compound's ability and tendency to absorb water directly from the air. It is a well-documented physicochemical mechanism reported in widely divergent research fields, such as dehumidification technology (Hassan & Hassan, 2008), atmospheric aerosol chemistry (Cruz & Pandis, 2000; Martin, 2000; Gupta et al., 2015), wood production (Peck, 1941), food preservation (Ayerst, 1965) and pharmaceutical engineering (Van Campen, 1980). Although hygroscopic properties are widely occurring, not all compounds remain solid but may liquify in contact with water vapour. Salts which become liquid are termed *deliquescent* and form a saturated solution if temperature and humidity conditions favour the phase transition (Mauer & Taylor, 2010). The consequences following the moisture absorption of a deliquescent salt, changing state, are, therefore, significantly greater than of a strictly hygroscopic compound which only increases its moisture content and mass.

Calcium nitrate and ammonium nitrate have, besides their propensity of absorbing moisture from the air, a great solubility and are both considered as highly soluble. According to the *CRC Handbook of Chemistry and Physics, 84th Edition* (Lide, 2004), $Ca(NO_3)_2$ has a solubility in water (1.44 g salt g^{-1} of water) four times larger than the one of sodium chloride (0.36). Ammonium nitrate has an even higher solubility (2.13), almost six times sodium chloride. To stabilise these sensitive salts while avoiding undesired effects like caking, shortened lifespan during storage and nitrogen losses in the field due to rapid dissolution, different coating and slow-release techniques have been introduced since the early 1930s (Herterich *et al.*, 1934). Although significant efforts have been made to reduce the hygroscopicity of fertilisers, there are still situations where quick dissolution is preferable such as during nitrogen feeding of high-quality cash crops by split application. In absence of rainfall, hygroscopic properties pose the only chance for a fertiliser solid to dissolve.

Calcium nitrate and ammonium nitrate occur in several fertiliser products and mixtures, often marketed for their high solubility and readily plant available nitrogen forms. Even though there has been much focus on developing high precision fertilisers, less is known about the dissolution rates of modern nitrogen fertilisers in the field after soil application due to hygroscopicity and deliquescence. While it is an unambiguous fact that precipitation and moist air make $Ca(NO_3)_2$ and NH_4NO_3 dissolve, still little is known about the actual dissolution dynamics. Dissolution rates as affected by hygroscopicity or rainfall were studied in this thesis.

1.2 Aim, objectives, and hypothesis

This thesis aims to improve our knowledge of how mineral nitrogen fertilisers based on $Ca(NO_3)_2$ and NH_4NO_3 dissolve in response to air humidity and rainfall. In this thesis, the dissolution rates of these two fertilisers were quantified through 1) water uptake by hygroscopicity and 2) water addition by rainfall. The objectives of the thesis are as follows:

i. To measure the dissolution rate of $Ca(NO_3)_2$ and NH_4NO_3-based mineral nitrogen fertilisers and of comparable pure chemical compounds by hygroscopic water uptake at high relative humidity (≥ 90 %).
ii. To measure the dissolution rate of the same fertilisers during precipitation at a moderate water intensity.
iii. To explain the measured dissolution rates with adequate literature.
iv. To assess plant availability of the fertilisers after dissolution

Based upon the objectives of this thesis, as well as the literature reviewed, the following hypotheses were formulated:

i. The difference in vapour pressure between a hygroscopic salt in solution and the surrounding air determines the hygroscopic rate. Salts having low vapour pressure absorb water quicker compared to those having a higher vapour pressure.
ii. Fertiliser products have lower hygroscopicity in relation to comparable pure chemicals, partly due to larger size and coating.
iii. The enthalpy of solution affects the hygroscopicity where salts having a high positive enthalpy of solution (dissolving endothermically) have higher hygroscopicity than those with a low enthalpy of solution.
iv. Dissolution rate of fertilisers by precipitation is mainly a function of solubility.

There is a need for an increased knowledge about fertilisers' dissolution, determining the need for rain and moisture, as well as the time required to dissolve and dilute a fertiliser. Aiming to pursue the objectives given above, fertiliser management can be improved, particularly when practicing split applications at any growth stage. Precision farming, not least that of fertilisation, has become important over the past decades but is not more precise than the precision in dissolution and plant availability of the nutrients. This thesis aims to provide some of that missing information.

2 Background

2.1 Mineral nitrogen fertilisers and their constituents

2.1.1 Production and formulation

Nitrogen-based mineral fertilisers have had an increasing importance in improving the productivity of the world´s arable land since their introduction in the early 1920s (Waggaman, 1922; Lu & Tian, 2017). In 1925, the worldwide production of synthetic nitrogen was 480 000 tonnes (Wilson, 1926) but would rise to 133 million tonnes in 2010, of which about 75 % used for fertiliser manufacturing (Smil, 2011). $Ca(NO_3)_2$ and NH_4NO_3 were early introduced on the fertiliser market but did not immediately succeed as they were almost impossible to handle without caking or dissolving (Beaumont & Mooney, 1925; Cox, 1932; Ross *et al.*, 1944). During the following decades, major engineering efforts were made to increase product quality by introducing new conditioning agents e.g. coating (Miller *et al.*, 1946) or by improving the manufacturing technology itself, gaining higher purity and drillability (Saeman *et al.*, 1952).

The very basis of the manufacturing of all mineral nitrogen fertilisers is the production of synthetic ammonia by the Haber process, also often called the Haber-Bosch

process (Haber & Rossignol, 1913). The ammonia gas produced in the Haber process can in a further step be led into a neutraliser, a large container where gaseous ammonia reacts with aqueous nitric acid to form a largely neutralised solution of NH_4NO_3 (Saeman *et al.*, 1952). To ensure the completeness of the neutralisation, the solution can, depending on the process design, be pumped into an additional tank where a final pH adjustment is performed (Saeman *et al.*, 1952). An evaporator is used to reduce the water content of the NH_4NO_3 solution to an acceptable level which differs depending on the solidification method chosen (European Fertiliser Manufacturers' Association, 2000). Solidification of fertiliser products can be performed either by prilling or granulation of the NH_4NO_3-concentrate. When prilling, droplets of uniform size crystallise while falling down a prilling tower, slowed by a rising air flow (Walters, 2006). Granulation, on the other hand, is a process where particles are linked together either by creating interparticle forces as in wet granulation (Hardesty & Ross, 1938) or by actively compacting a dry powder under high pressure (Hignett, 1985). To ensure stability and storability of the products, the prill or granule is coated with an adequate conditioning agent, usually, mineral oil based, during the final step in the fertiliser manufacturing (Miller *et al.*, 1946; Rindt *et al.*, 1968).

Ammonium nitrate has become one of the most frequently used nitrogen fertilisers with nitrogen contents up to 35 % by mass and is often mixed with other nutrients, receiving multi-nutrient fertilisers e.g. NP and NPK (Gorbovskiy *et al.*, 2017). It is also a major constituent in several nitrogen-based blends, often mixed with small amounts of sulphur or magnesium and marketed under trade names as NS 26-14, NS 27-4, NS 30-7 or N27 by manufacturers like Uralchem, Borealis, Eurochem, and Yara. Ammonium nitrate can also be mixed with calcium carbonate forming $Ca(NO_3)_2$ in the reaction: $CaCO_3 + 2NH_4NO_3 \rightarrow Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O$ (Kiiski, 2009). Another common nitrogen fertiliser, confusingly termed "Calcium nitrate", is CAN or calcium ammonium nitrate, which is produced either by reacting a concentrated $Ca(NO_3)_2$-melt with ammonium nitrate, forming the hydrated crystalline double-salt $5Ca(NO_3)_2*NH_4NO_3*10H_2O$ (Nikolaisen, 1990) or simply by

mixing a calcium powder e.g. dolomite with NH_4NO_3 followed by granulation (Van Hijfte & Goethals, 1982). Thus, the properties of CAN fertilisers may differ greatly depending on their formulation and NH_4NO_3 content. For the sake of clearness, calcium nitrate refers strictly to $Ca(NO_3)_2$ and CAN to $5Ca(NO_3)_2*NH_4NO_3*10H_2O$ in this thesis.

2.1.2 Properties of calcium nitrate and ammonium nitrate

The calcium nitrate salt may, the anhydrate excluded, occur as three hydrates: $Ca(NO_3)_2*2H_2O$; $Ca(NO_3)_2*3H_2O$; $Ca(NO_3)_2*4H_2O$, of which the latter, the tetrahydrate, represents the stable solid phase at room temperature (Bassett & Taylor, 1912). Having a various number of water of crystallisation, the physicochemical properties, e.g. melting point and solubility, differ between the hydrates (Bassett & Taylor, 1912; Ewing *et al.*, 1927). As can be seen in Table 1, the water of crystallisation has a major impact on the behaviour of the salt, lowering the melting point while increasing the solubility.

Table 1. *Physicochemical properties of NH_4NO_3 and $Ca(NO_3)_2$ and its respective hydrates.*

Salt	Melting point	Solubility (g salt 100 g^{-1} solution)		Reference
	(°C)	Temp (°C)		
$Ca(NO_3)_2$	561	25	77.30	Taylor & Henderson, 1915; Lide, 2004
$Ca(NO_3)_2*2H_2O$	[1]) 48.4-51.3			Bassett & Taylor, 1912
$Ca(NO_3)_2*3H_2O$	51.1			Bassett & Taylor, 1912
$Ca(NO_3)_2*4H_2O$	42.7	20	130.90	Bassett & Taylor, 1912; Lide, 2004
		25	143.90	Lide, 2004
		30	155.80	Lide, 2004
NH_4NO_3	169.6	20	185.70	Lide, 2004; Kiiski, 2009
		25	212.50	Lide, 2004
		30	236.70	Lide, 2004

[1]) Only exists within the reported interval, no true melting point found (Bassett & Taylor, 1912)

The phase transition of the melting salt from solid to saturated solution, at the temperatures reported above, can be described as $Ca(NO_3)_2*XH_2O \rightleftharpoons Ca(NO_3)_2 + XH_2O$ (Ewing *et al.*, 1927). If dissolved in water, $Ca(NO_3)_{2(s)}$ can further dissociate into $Ca^{2+}_{(aq)}$ and $2NO_3^-{}_{(aq)}$ (Sharpe, 2018). Since $Ca(NO_3)_2$, by nature, is endothermic and consumes heat when dissolved in water, the rate at which $Ca(NO_3)_2$ dissolves increases with rising temperature (Tyrer, 1911). Thereby, $Ca(NO_3)_2$ has a greater solubility in warm than in cold water (Lide, 2004).

Ammonium nitrate forms during the exothermic reaction of ammonia and nitric acid: $NH_{3\ (g)} + HNO_{3\ (aq)} \rightarrow NH_4NO_{3\ (s)}$ (Kiiski, 2009) and dissociates endothermically into $NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$. Unlike $Ca(NO_3)_2$, there are no hydrates formed but five known crystalline phases (I-V), of which the orthorhombic phase, NH_4NO_3-IV, is the stable crystal structure at room temperature (Bowen, 1925; Oommen, 1999). Ammonium nitrate is highly soluble and its solubility increases with temperature (Table 1). The solubility of NH_4NO_3 is also higher than of $Ca(NO_3)_2$ at the same temperature.

2.2 Hygroscopicity and deliquescence

2.2.1 Hygroscopic moisture absorption

Hygroscopic absorption of water occurs when the vapour pressure of the surrounding air exceeds the vapour pressure at the surface of a solid salt or salt solution (Yee, 1944). The addition of a hygroscopic salt to a pure water will always lower the vapour pressure of the aqueous salt solution that forms. Therefore, a solution of a dissolved hygroscopic compound will, at certain vapour pressures, absorb air moisture. The hygroscopic effect increases with increasing salt concentration, while it, conversely, levels off with degree of dilution (Adams & Merz, 1929). Thus, the

magnitude of hygroscopicity, at a given temperature, is proportional to the difference between the vapour pressure of a solid or a salt solution and that of the surrounding air. For every hygroscopic salt and fertiliser mixture, there is a certain vapour pressure and a corresponding relative humidity (RH_0), defining the equilibrium between solid and liquid. That relative humidity, at a certain temperature, corresponds to the ratio between the vapour pressure of a salt solution at saturation (P_{salt}) and the pressure of the surrounding water vapour (P_s) according to the following (Piqué *et al.*, 1992):

$$RH_0 = \left(\frac{P_{salt}}{P_s}\right) * 100 \quad \text{(equation 1)}$$

A relative humidity (RH) above RH_0 favours the liquid phase, where moisture is absorbed, whilst the salt stays dry and solid for all RH values below RH_0 (Mauer & Taylor, 2010). Adams & Merz (1929), who measured vapour pressures over saturated fertiliser solutions, reported RH_0 values for several common fertilisers and mixtures of which $Ca(NO_3)_2*4H_2O$ and NH_4NO_3 are reproduced in Table 2. They found RH_0 for the two fertilisers to be 50.5 and 62.7 %, respectively, at 25 °C. At humidity levels above those values, both fertilisers are likely to absorb water or even dissolve. Repeating the procedure using fertiliser mixtures, Adam & Merz (1929) further discovered salt mixtures generally being more hygroscopic than the most hygroscopic constituent.

As can be seen in Table 2, mixing NH_4NO_3 with $Ca(NO_3)_2*4H_2O$ reduces the relative humidity required for absorption at 30°C. Interestingly, less moisture in the air is required for dissolution of the mixture than of the single constituents. There are,

Table 2. *Relative humidity at which fertilisers start to absorb moisture from the air (temperature interval of 15-40°C). The table is based on data from Adams & Merz (1929).*

	Relative humidity (%) at different temperatures				
Temperature °C	15	20	25	30	40
$Ca(NO_3)_2*4H_2O$	55.9	55.4	50.5	46.7	35.5
NH_4NO_3	69.8	66.9	62.7	59.4	52.5
$NH_4NO_3 + Ca(NO_3)_2*4H_2O$				23.5	

however, also a few exceptions including Cal-urea (calcium nitrate and urea combined as $Ca(NO_3)_2*4CO(NH_2)_2$) and the combined ammonium nitrate and ammonium sulphate salt $(NH_4)_2SO_4$-$2NH_4NO_3$ resulting in a higher vapour pressure, and thus, less hygroscopic properties (Adams & Merz, 1929). Moreover, the results of Adams & Merz (1929) show a strong temperature dependence where rising temperatures allow hygroscopicity to occur at lower relative humidities. Edgar & Swan (1922), also measuring vapour pressures of several hygroscopic fertilisers, suggested the rate of hygroscopic moisture absorption to be affected by the velocity of air surrounding the solid in question, the surface of the solid, and finally, a certain reaction constant representing the specific properties of the salt. The effect of surface properties was further discussed by Keenen (1939) where particle size and density of hygroscopic contact points were thought to affect the rate of moisture absorption. Moreover, the concentration of soluble salts in a fertiliser product was shown to have a substantial effect on the absorption rate, increasing in mixtures with more soluble nitrogen (Keenen, 1939).

2.2.2 Deliquescence

Deliquescence is defined as the melting or liquification of a salt by the absorption of atmospheric water, resulting in the phase transition from solid to liquid (Webster, 1831). It should not be confused with hygroscopicity, which means uptake of gaseous water and, per definition, does not include any phase transition. Research related to deliquescence was established long ago, e.g. the deliquescence of NH_4NO_3 was examined already in the work by Kortright (1899), more than one hundred years ago, and the deliquescence of $Ca(NO_3)_2$ was discussed and defined by Baynes (1888). Based upon vapour pressure measurements of Edgar & Swan (1922) and Adams & Merz (1929), the point at which deliquescence occurs has been defined as the vapour pressure and corresponding relative humidity at which hygroscopicity begins (RH_0). Thereby, deliquescence is the parallel dissolution following the hygroscopic moisture absorption of a deliquescent salt (Cruz & Pandis, 2000). Piqué

et al. (1992) summarised the melting reaction of $Ca(NO_3)_2 * 4H_2O$, in presence of water, by the reaction of: $Ca(NO_3)_2 * 4H_2O + H_2O \leftrightarrow$ saturated solution.

A phase transition must be thermodynamically favourable in order to take place. As previously mentioned, water of crystallisation lowers the melting point as shown for $Ca(NO_3)_2$. However, water molecules sorbed at the surface of a deliquescent salt also lower the melting temperature and if enough water is sorbed, the melting point is lowered to one below room temperature and the salt conclusively melts (Lagassé, 2000; Meng *et al.*, 2016). The potential for phase transition of a deliquescent salt has thermodynamically been expressed by Mauer & Taylor (2010) as:

$$\mu_s - \mu = RT * ln\left(\frac{p_s}{p_0}\right) \quad \text{(equation 2)}$$

where μ_s and p_s refer to the chemical potential and vapour pressure of a saturated salt solution, and where μ and p_o are the chemical potential and vapour pressure of pure liquid water in equilibrium with its own vapour, R is the gas constant and T the temperature of the system. As the chemical potential ($\mu_s - \mu$), also Gibb´s free energy, is negative for $p_s < p_o$, the liquid phase will be favoured as long as the vapour pressure difference prevails. As for hygroscopicity, the larger difference in vapour pressure or the higher relative humidity above RH_0, the faster is the deliquescence of the salt (Mauer & Taylor, 2010). As seen in Figure 1, the deliquescence of a salt can be described in four steps. Step 1 shows the dry salt crystal where the RH is below RH_0. Even though the salt is considered solid, a thin layer of water molecules is present at the solid surface by adsorption (Mauer & Taylor, 2010). With increasing RH and concentration of gaseous water molecules surrounding the salt, more vapour adsorbs to the surface. However, rarely more than 4-5 molecular layers can be adsorbed (Chen, 2009). In step 2, RH equals or exceeds RH_0 whereupon a thin saturated solution starts to cover the surface (Mauer & Taylor, 2010; Tereshchenko, 2015). Besides defining the point of deliquescence, RH_0 also defines the shift in sorption type from adsorption of water molecules at the surface to absorption of vapour into the bulk solution (Tereshchenko, 2015). As shown in step 3, the saturated solution continuous to absorb water vapour that condensates the liquid surface

which becomes thicker. This absorption dilutes the solution whilst the dilute solution, parallelly, starts to dissolve the solid core (Keenen, 1939; Tereshchenko, 2015). Having reached a completely dissolved solid core and saturated solution in step 4, the amount of water in the system is equivalent to the solids solubility in it (Tereshchenko, 2015). Thereafter, the solution continues to absorb vapour as long as $p_s < p_o$ or until the solution reaches a dilution, so large, that there is no vapour pressure difference left in the system (Adams & Merz, 1929).

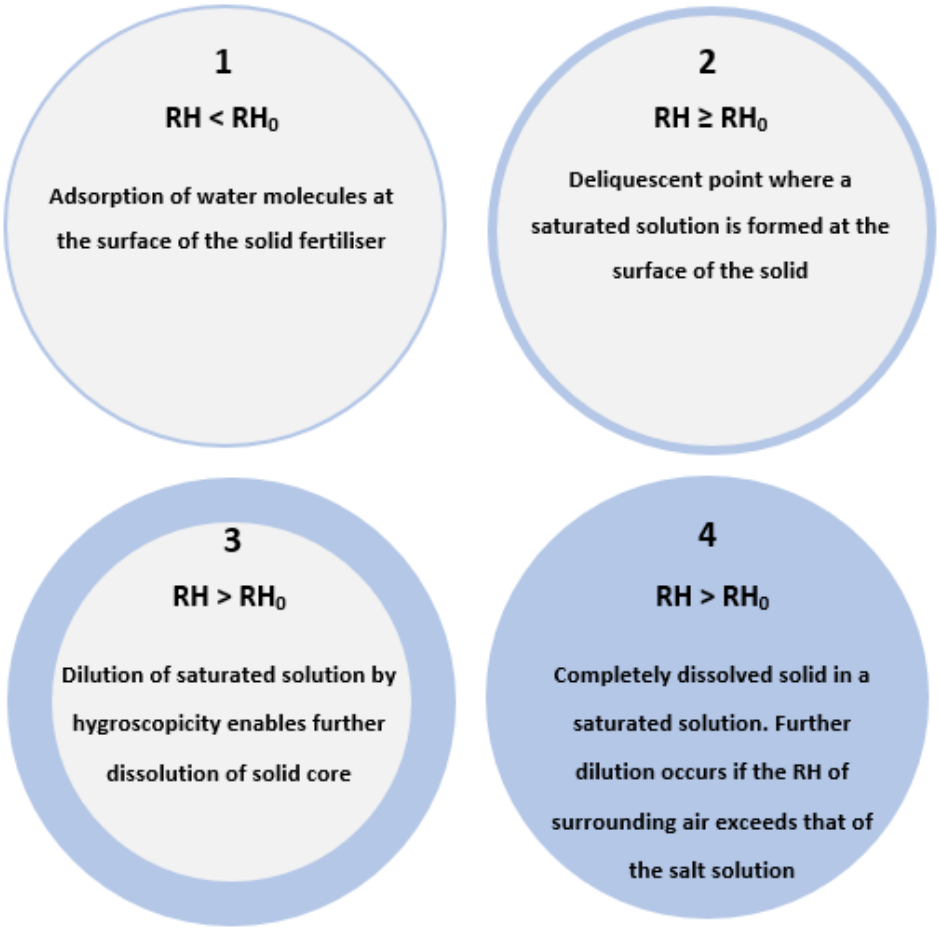

Figure 1. Illustration of the step-wise deliquescence of a solid in presence of water vapour at different relative humidities (RH). At RH values above the deliquescent point (RH_0), the solid dissolves to a saturated solution which in turn dilutes by hygroscopicity. Blue colour represents the dissolved phase and grey the solid. The drawing is based upon the illustrations of Mauer & Taylor (2010).

2.2.3 Enthalpy of solution and endothermic properties of fertilisers

One of the most fundamental, but also the least discussed issue in the literature of hygroscopicity and deliquescence, is how the change in temperature during dissolution affects the rate of moisture absorption. Salts like ammonium nitrate, calcium nitrate tetrahydrate and urea dissolves endothermically and immediately chill the water they dissolve in. It is well known that a warm water vapour condenses a cold liquid surface as the vapour pressure of a cold liquid is lower. It therefore seems reasonable to believe that the rate of hygroscopicity and deliquescence could be a function of a solid's capacity to generate coolness when dissolving. This could eventually be proved by reversing back to the thermodynamics of deliquescence and equation 2 with chemical potentials $\mu_s - \mu$ representing the change in Gibbs free energy when temperature and pressure are held constant (Leribaux, 1976; Job & Herrmann, 2006). The change in free energy (in its standard state) further relates to the change in enthalpy and entropy according to:

$$\Delta G° = \Delta H° - T\Delta S° \quad \text{(equation 3)}$$

where ΔG is the Gibbs free energy change, ΔH the enthalpy change, T the temperature and ΔS the change in entropy (Alberty, 1969; Cvitas, 2007). If deliquescence occurs spontaneously, ΔG must be negative. However, ΔG itself, does not tell the dissolution rate in the system solid-saturated solution. Instead, the change in enthalpy, could in terms of kinetics, be more interesting as it declares whether the deliquescence of a solid is endothermic or exothermic i.e. if heat is absorbed or released. In this study, all chemicals tested dissolve endothermically, having positive ΔH-values and thereby lower the temperatures of the final solutions. It therefore seems likely that the enthalpy of solution may affect the rates of deliquescence.

2.3 Coating agents

Coatings of particles and agents used for coating of deliquescent materials have extensively been studied and evaluated, such as for atmospheric aerosols (Andrews & Larson, 1993), explosives (Gilliland, 1959), rocket propellants (Oommen, 1999; Yang *et al.*, 2017), pharmaceuticals (Zelkó & Szakonyi, 2012) and mineral fertilisers (Sharma, 1979). Coating of fertilisers was introduced already in the early 1940s by the American manufacturer Hercules Powder Company, developing a rosin-paraffin coating used for ammonium nitrate fertilisers (Miller *et al.*, 1946), which was further modified and used for controlled release of the main constituent (Kakoulides & Valkanas, 1994). The early coating normally comprised of mineral oil or paraffin, reducing the polarity and thereby the hygroscopicity of the fertilising salts, and followed by a cover of dust, protecting the product against caking (Miller *et al.*, 1946). Sulphur coating was also introduced (Sharma, 1979) and Rindt *et al.* (1968) and Pettygrove (1977) studied the slow release of sulphur coating when used on urea fertilisers.

Polymer coating techniques have been reviewed in several publications (Devassine *et al.*, 2002; Tomaszewska & Jarosiewicz, 2002; Costa *et al.*, 2013). Detmer *et al.* (1968) were amongst the first to patent a method of polymer coating suitable for fertiliser use. Since then, polymer coating techniques have advanced substantially and are mostly used for encapsulation of fertilisers to control nutrient release (Hargrove & Detrick, 2002; Noppakundilograt *et al.*, 2015; Giroto *et al.*, 2017). Nevertheless, the more traditional way of coating, mixing mineral oil, waxes, and resin in various proportions, remains important for stabilisation and storage of solid fertilisers and new recipes and additives are continuously developed (Obrestad *et al.*, 1993; Obrestad & Tande, 2017). This type of coating is especially suitable for non-control release fertilisers and covers a substantial part of ammonium nitrate and calcium nitrate blends on the market, e.g. Tropicote™ marketed by Yara International.

The quality of coating materials and uniformity of coating is crucial to avoid cracks and maintain a proper protection against undesired moisture absorption or deliquescence (Sharma, 1979). Measuring dissolution rates, Brown *et al.* (1966) found that nutrient release rates from urea were reduced with increasing thickness of resin surrounding the fertiliser. The quantitative effect of coating on hygroscopicity was documented in a patent by Obrestad *et al.* (1993), where coated (Tropicote™) and uncoated samples of NH_4NO_3 and CAN were exposed to 70 % RH at 25°C and 67 % RH at 20°C, respectively. After 5 hours, the conditioning agent in question had reduced the moisture absorption of NH_4NO_3 by 34 % compared to the uncoated one. The reduction was even larger for CAN, accounting for 58 % reduction relative to the uncoated sample. In summary, coating has a substantial positive effect on the technical properties of mineral fertilisers.

2.4 Theoretical approaches to dissolution measurements

2.4.1 Dissolution rate in moist air

The literature reviewed in the previous sections demonstrates that $Ca(NO_3)_2$ and NH_4NO_3 are highly sensitive to high relative humidities and are likely to dissolve spontaneously. It is also clear that the rate of deliquescence increases with rising temperature and higher relative humidities. The maximum dissolution rate of a deliquescent salt at room temperature should, therefore, occur at RH-values close to 100 %.

Hygroscopicity of fertilisers can be estimated measuring the weight gain over time under humid conditions as shown for technical ammonium nitrates (Harris, 1970). There are, however, no publications connecting moisture absorption rates of deliquescent salts to their dissolution dynamics. Under constant conditions, the transition from solid phase to a saturated solution of a deliquescent salt is equal to the solubility of that salt in water. A fertiliser salt is therefore defined completely dissolved when the moisture absorbed equals the inverse of its solubility in water.

2.4.2 Dissolution rate at precipitation

There is little or no research concerning the dissolution of mineral fertilisers as affected by precipitation. Nonetheless, the mechanisms of rain-initiated dissolution ought to be simple and primarily a function of the number of droplets hitting the granule causing the fertiliser to dissolve. The solubility, in turn, increases with rising temperature why also the dissolution rate is likely to be higher with rising temperature of the water droplets. As rainfall and high relative humidity coincide, hygroscopic moisture absorption may also, in parallel with rain, help to dissolve the fertiliser. However, at intense rainfall, the hygroscopic effect is likely to be neglectable as so much water is added by precipitation.

A fertiliser salt, when dissolved in a sufficient amount of water, dissociates into its free ions and the concentration of those can be estimated by measuring the conductivity. The degree of dissolution of a fertiliser at a certain point, can, therefore, be estimated by recording conductivity, i.e., the portion of charged particles in the solution it has dissolved in.

3 Material and methods

The experimental work was performed in two separate studies described in the chapters below. One study aimed at recording the dissolution dynamics of $Ca(NO_3)_2$ and NH_4NO_3-based fertilisers and of comparable pure chemicals by absorption of water from moist air, and the other to study the dissolution dynamics under addition of rainwater. The compounds were exposed to moist air and their hygroscopic absorption capacity and deliquescence were measured. The amount of water required to dissolve the fertilisers was determined in a rain simulator.

3.1 Determination of hygroscopicity and deliquescence

3.1.1 Design of experiment, resources, and chemicals

The experiment was conducted in an enclosed room where humidity and temperature were controlled and kept constant at 90-99 % RH (but below condensation) and 25°C ± 1°C, respectively. The enclosed room had a volume of 17 m^3 and was tempered and humidified by tepid water kept in 15 open plastic containers, covering 2.5 m^2. The temperature was held with an immersion heater and the temperature and humidity conditions were monitored with an RH30 combined digital thermo-hygrometer (Extech Instruments). The humidifying system was, by calculation, designed to passively supply 10 grams of a deliquescent salt with sufficient water, allowing it to dissolve within an hour without lowering the RH of the room with

more than 0.6 %. Besides the immersion heater, an electric heater, air cooler, and fan were used, when needed, to maintain stated conditions.

Two $Ca(NO_3)_2$ and NH_4NO_3-based fertilisers manufactured by Yara International were used in the experiment (Table 3). $Ca(NO_3)_2$ was represented by YaraLiva®Kalksalpeter™, also marketed as YaraLiva®Tropicote™ in the British Isles. Yet, it is, strictly speaking, not a $Ca(NO_3)_2$ fertiliser but a CAN with minor proportions of NH_4NO_3. NH_4NO_3, in turn, was represented by YaraBela®Axan™ (NS 27-4), also sold under the same trade name globally (with minor modifications). The chemicals chosen were supplied by VWR Chemicals and of high purity (≥98 %). The details and properties of the chemicals are listed in Table 4.

Table 3. *Overview of the fertilisers used in the experiment, their formula, components, and physicochemical properties.*

Type of fertiliser	YaraLiva®Kalksalpeter™	YaraBela®Axan™
Name	Calcium Ammonium Nitrate	Ammonium Nitrate
Formula	$5Ca(NO_3)_2*NH_4NO_3*10H_2O$	NH_4NO_3
Active component (%)	≥90 - <100	≥70 - <80
Other ingredients	none	0.6 % Mg, 3.7 % S
Density (g/cm^3)	1.1	1
Solubility (g/g H_2O at 25°C)	2.5	[1)]2.125

[1)] No specific solubility value is available for the fertiliser product. The solubility of YaraBela®Axan™ is assumed to follow that of NH_4NO_3 reported in the previous chapter (Table 1).

Table 4. *Overview of the comparable pure chemicals used in the experiment, their formula, and physicochemical properties.*

Type of chemical	Calcium nitrate tetrahydrate	Ammonium nitrate
	GPR RECTAPUR®	AnalaR NORMAPUR® ACS
Manufacturer	VWR Chemicals	VWR Chemicals
Chemical	Calcium nitrate tetrahydrate	Ammonium nitrate
Formula	$Ca(NO_3)_2*4H_2O$	NH_4NO_3
MW	236.15	80.04
Purity (%)	99.4	99.5
Density (g/cm^3)	1.86	1.73
Solubility (g/g H_2O at 25°C)	[1)]1.439	[1)]2.125

[1)] The solubility is assumed to follow the values reported in the *CRC Handbook of Chemistry and Physics, 84th Edition.*

Metal nets were used for the dissolution procedure where compounds were applied over the net surface with plastic cups attached beneath, collecting the dripping saturated salt solution. Regularly and according to a schedule, the nets were weighed on a scale and the weight increase over time was recorded. Four replicates were used for each fertiliser and chemical. The metal nets used had a mesh size of 0.5 mm and were made of stainless steel whilst the plastics glued to the net came from 50 ml centrifuge tubes. The nets were resting on stands over a free water surface. A digital scale, A&D HF-2000G (A&D Company, Limited) was used to record the weight increase with two digits reading accuracy.

3.1.2 Procedure

Fifteen uniform fertiliser granules in the size range of 3 - 4.5 mm with an approximate weight of 0.6 g were used in each treatment. The procedure was repeated for both fertiliser products in four replicates and the individual weights (two digits) of each run were noted (Appendix 1). The granules were distributed over the net in five groups of three granules each. The chemicals were, due to their fine powdered texture and tendency to stick to surfaces, weighed in two steps. First, a total of about 0.75 g of each chemical was weighed and put in small centrifuge tubes and stored dry. This was also done in four replicates for each treatment. The tubes were then emptied over the net at five sites with a plastic collector attached beneath and the total net-weight was recorded before and during the experiment (Appendix 1). The weight was recorded according to a schedule shown in Figure 2.

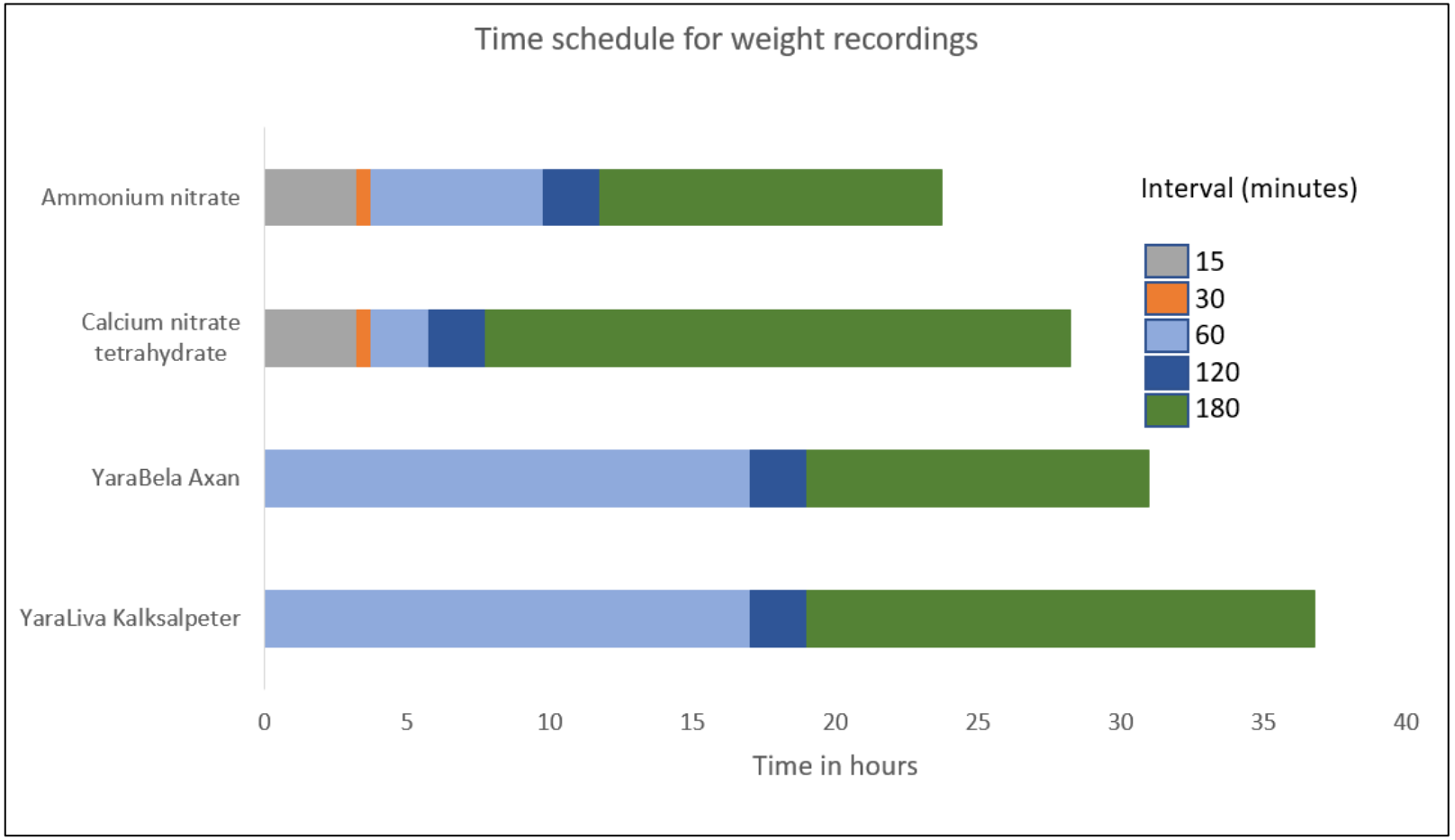

Figure 2. Total measuring period and weighing intervals during the hygroscopicity experiment. Fertilisers were initially weighed once an hour, compared to the pure chemicals which were weighed every 15 minutes. Due to practical reasons and the fact that the moisture absorption in most cases was more intensive in the start of the experiment, fertilisers and salts were weighed less often in the end of the experiment.

In order to record the kinetics of dissolution, measurements were made most frequently during the initial part of the experiment. Pure chemicals and fertilisers were weighed at intervals between 15 minutes and 3 hours. The intervals were based upon pre-measurements where hygroscopic moisture absorption and dissolution rates were roughly estimated over a period of two days.

3.1.3 Calculations

Having recorded the increase in weight of fertilisers and chemicals, the hygroscopicity at a certain time could be expressed as:

$$Hygroscopicity\ (H) = \frac{m_a}{m_s} \quad \text{(equation 4)}$$

where m_a is the mass of water absorbed and m_s mass of solid at the start of the experiment. Accordingly, an H of 0.8 means that 1 gram of solid has absorbed 0.8 grams of water. The rate at which hygroscopicity proceeds can further be expressed as:

$$H_{rate} = \frac{\Delta H}{\Delta t} \quad \text{(equation 5)}$$

where H is hygroscopicity and t is the time in hours. Although fertilisers and chemicals may have the same H_{rate}, gaining an equal amount of water over time, the consequences may still differ when considering their respective solubility. As stated in previous chapters, a deliquescent salt is completely dissolved when H equals the inverse of its solubility. Thereby, a salts sensitivity for moist air does not only depend upon H, but also on its solubility in water. The deliquescence (D) of a salt and its following hygroscopic dilution would, by the same logic, be possible to describe as:

$$D = \left(\frac{\frac{m_a}{m_s}}{\frac{1}{s}}\right) \quad \text{(equation 6)}$$

where s is solubility (grams of solute per gram of water). The deliquescence moreover corresponds to the percentage of dissolution or dilution according to the following:

$$Percent\ dissolution\ or\ dilution = D * 100 \quad \text{(equation 7)}$$

Using equation 6, where m_a is set to 0.5, m_s and s to 1.2 and 1.5, respectively, D becomes 0.625 which means that the solute has absorbed 62.5% of the amount of water it needs to dissolve, or that it is to 62.5 % dissolved. If m_a, m_s, and s are set to 1.8, 1.2 and 1.5, D becomes 2.25 meaning that the solute gone completely dissolved, and additionally, been diluted with 125 %. The rate of D, as a function of time, can in a similar way to H_{rate} be expressed as:

$$D_{rate} = \left(\frac{\frac{\Delta m_a}{m_s}}{\frac{1}{s}} \right) * \frac{1}{\Delta t} \quad \text{(equation 8)}$$

3.1.4 Calculations for quantifying the effects of endothermic dissolution on vapour pressure and hygroscopicity

Assuming a saturated solution to form at the surface of a solid when deliquescence occurs, the vapour pressure above that solution would follow the recordings of Adams & Merz (1929). Moreover, the temperature change caused by the dissolution of any salt can be estimated according to:

$$\Delta H = -cm\Delta T \quad \text{(equation 9)}$$

where ΔH is the change in enthalpy, c is the specific heat capacity of water (4.18 kJ kg^{-1} $^oC^{-1}$), m is the mass of water (kilograms) and ΔT is the temperature change. Rewritten and rearranged, the temperature change is given by:

$$\Delta T = \frac{\Delta H}{-cm} \quad \text{(equation 10)}$$

According to the equation, the temperature change increases with decreasing mass of water the solid dissolves in. This is, however, only true to some point as the ΔH-value refers to the change in enthalpy when a solid dissolves in an infinite amount of water (Lide, 2004). The equation given above, is, thereby, less likely to describe the immediate temperature decrease occurring when any of the salts used forms a saturated solution.

To quantify the endothermic effects on the vapour pressure when dissolving any of the fertilising salts, a non-saturated solution consisting of 1 gram of solute in 5 grams of solvent (water) was used to represent a saturated solution in equation 10 as a higher concentration, in practice, wouldn't lower the temperature much more.

Thereby, assuming a saturated solution to cool equally to a non-saturated solution of the ratio presented above, the vapour pressure lowering when endothermically dissolving ammonium nitrate, calcium nitrate tetrahydrate and calcium ammonium nitrate decahydrate (Kalksalpeter™), in water, could be estimated.

Calculations were made in two scenarios. First, the vapour pressures of saturated solutions kept at 25°C were tabulated for ammonium nitrate and calcium nitrate tetrahydrate according to the results of Adams & Merz (1929), representing a scenario where no vapour pressure lowering other than by the salt itself occurred. Next, the endothermic effect was investigated by calculating the temperatures of each solution when mixing the solids in water having an initial temperature of 25°C. Interpolating the vapour pressures at the calculated temperatures from the recordings of Adams & Merz (1929), both the temperature effect and the combination effect of temperature and salt concentration on the vapour pressure could be evaluated. Axan™ was throughout the calculations assumed to follow ammonium nitrate.

3.2 Determination of dissolution by precipitation

3.2.1 Design of experiment, resources, and chemicals

The experiment was performed in a rain simulator, exclusively built and designed for the study. The rain simulator used comprised of two units, a sprayer unit and an electric control device (Fig 3). The sprayer unit consisted of a frame upon which a pressure sprayer was placed, centered over a module in which the dissolution of the fertilisers occurred.

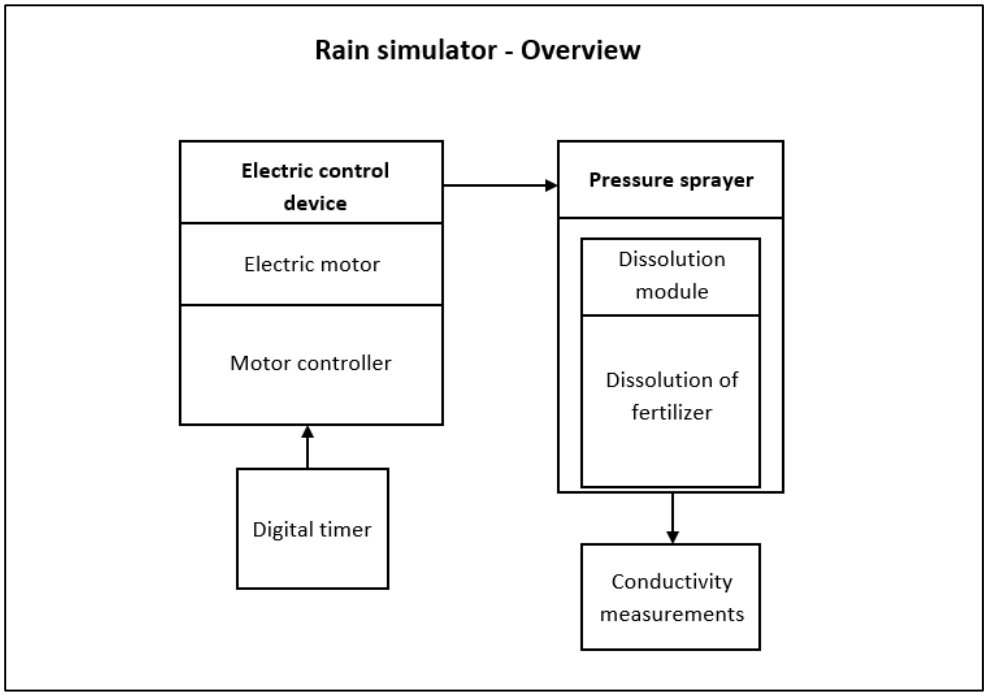

Figure 3. An overview of the rain simulator used in the experiment showing the two major units in bold, an electric control device regulating the pressure sprayer that simulates the rainfall. The leachate water leaving the pressure sprayer box was further analysed for its conductivity.

The module shown in Figure 4, in turn, comprised of a 15-cm high PVC pipe (1) (Ø10.5cm) which was placed upon a net and kept in place by a positioner (2). The net (3) was made of stainless steel and had a mesh size of 0.5 mm. Fertiliser granules were put on the net within the area defined by the pipe and frequently sprayed with deionised water. The number of mm rain was estimated as the volume of water sprayed into the module divided by the defined area. Beneath the net, a collector caught the rain droplets and the dissolved fertiliser salt (4). The base of the collector was sloping and the water entering it was further led into a drainage pipe in the very bottom (5). The leachate water leaving the module was analysed for its salt content.

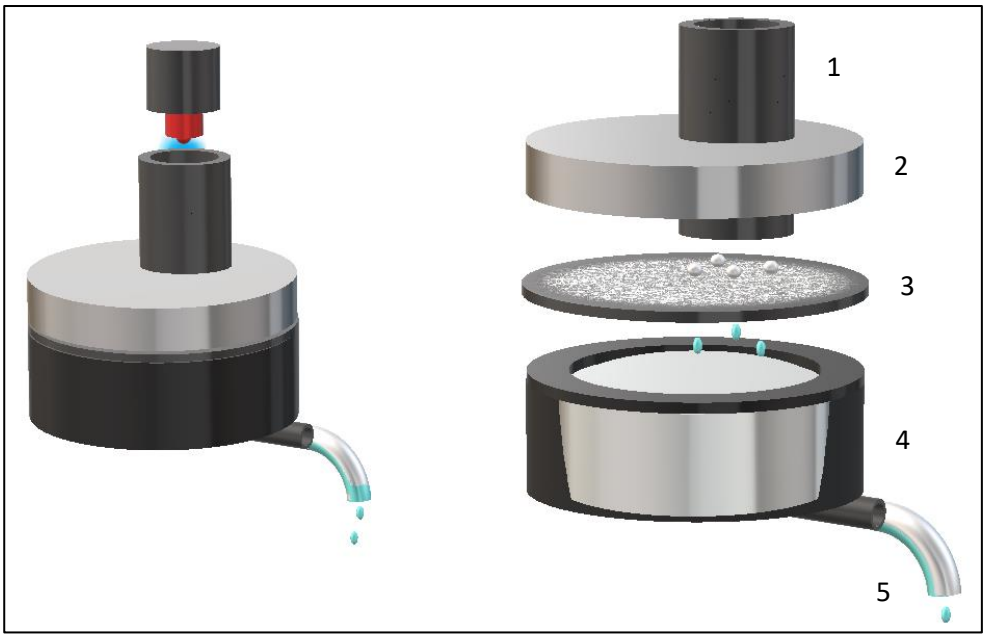

Figure 4. A blueprint of the module in which the dissolution of the fertiliser granules occurred. First, water was sprayed from the top of the pipe (1). The droplets hit the granules on the net (3) and dissolved the fertiliser. The leachate was collected (4) and drained (5) before it was analysed for its salt content.

The pressure sprayer was mechanically regulated by an electric motor unit. The motor unit was, in turn, regulated by a built-in motor controller and additionally managed by an external digital timer device (Fig 3). When running automatically, the highest frequency of water sprayed in the rain simulator was every second minute. Each spray lasted for three seconds and the minimum amount of precipitation possible, at that time, was about 0.2 mm (low pressure).

In the rain simulation, only fertilisers were used as the fine powder textured chemicals immediately would dissolve if spraying them. YaraLiva®Kalksalpeter™ and YaraBela®Axan™ were chosen, as they were in the previous hygroscopicity test (see Table 3 for properties). The conductivity measurements were made with an inoLab Cond 720 laboratory conductivity meter (WTW) and the values automatically temperature compensated (25°C). All fertiliser samples were weighed with the previously used scale (A&D HF-2000G), and with two digits accuracy.

3.2.2 Procedure of rain simulation

An amount of 0.6 grams of each fertiliser, all granule size fractions except damaged ones included, were weighed and evenly distributed over the net in the fertiliser dissolution module. The weight and number of fertiliser granules in the samples were recorded individually (Appendix 3) and each treatment had five replicates. The module was put in the simulator and the sprayer was adjusted to give approximately 0.6 mm of rain in each rain shower every second minute. The rain simulation started with a spray and a first leachate sample was immediately collected in a 250-ml glass bottle. The collector and drainage were flushed with about 100 ml of water into the same glass bottle to remove all salt and dilute the leachate. The temperature of the water used was 21.6°C ± 0.5°C.

All water added and collected was stepwise and carefully weighed to specify the individual contributions and the exact amount of precipitation. The procedure was repeated 20 times for Kalksalpeter™ and 25 times for Axan™, both in intervals of two minutes, giving a total of 20 and 25 leachate samples, respectively. An aliquot (about 35 ml) of each leachate sample was transferred to a 50-ml centrifuge tube and analysed for its salt content by conductivity measurements. The tubes were standing for at least one hour to ensure complete dissolution before conductivity was measured directly in the tubes. Pure deionised water was used as a control, to make sure that no factor, other than the dissolution of the fertiliser, did affect the conductivity readings.

3.2.3 Calculations

Conductivity values were converted into concentration data (ppm) by using a conversion factor. As the relation between an electrolyte's concentration and conductivity is linear, the factor, also known as k in $y = kx + m$, was determined for each fertiliser by establishing a standard curve by preparing various solution concentrations (Appendix 2). Four different concentrations were used with four replicates

each and the conversion factor was found to be 1.157 and 1.473 for Kalksalpeter™ and Axan™, respectively. The complete equation of the conversion of a conductivity to the mass of salt in a sample could be expressed as:

$$m_s = \frac{\sigma * 0.001 * V}{X} \quad \text{(equation 11)}$$

where m_s is the mass of salt in grams, X the conversion factor (also known as k), σ the conductivity in µS/cm and V the volume in liters of the solution analysed. The degree of dissolution of a fertiliser, at a certain point (time t), can further be considered as:

$$\%\ dissolved\ solid = \left(\frac{m_{cum(t)}}{m_{end}}\right) * 100 \quad \text{(equation 12)}$$

where $m_{cum(t)}$ is the cumulative mass of salt, drained up to the time t and where m_{end} is the sum of all salt contents leached up until the end of the simulation.

3.2.4 Determination of non-toxic salt concentrations for plants

Dissolution of a fertiliser will contribute to the salinity of a system. The salinity is defined by its electrical conductivity (EC_e) given in dS/m and high salinities are often associated with adverse impacts on crop growth and health. Amacher *et al.* (2000) reported threshold values for numerous agricultural crops above which the plant starts to lose yield, values which in this thesis been used to estimate the dilution need (Table 15 in the result chapter). Among cereals, wheat was the most sensitive against salinity, having a threshold value of 4.7 dS/m, followed by oats (5.2 dS/m). Barley had the highest salt tolerance with a threshold value of 8.0 dS/m. In the dilution calculations, wheat and barley were chosen as they represent the least and the most salt tolerant cereals.

Using the conversion factors of Kalksalpeter™ and Axan™ (1.157 and 1.473, respectively), the threshold conductivity values for toxicity were recalculated into concentrations in g salt/kg water by using equation 11. The additional amount of water required for an adequate dilution of the solutions could thereby be estimated. The volume of water needed to reach a non-toxic dilution of the two respective

fertilisers was calculated in two scenarios referring to saturated and unsaturated conditions, respectively. The latter was based upon the concentration salt measured in the leachate collected during the rain simulation.

3.3 Data analysis

Data analysis was based on mean values of 4 or 5 replicates for each treatment and variations within treatments were presented as standard deviations. The kinetics of hygroscopicity and dissolution were plotted, and data were fitted to mathematical functions. This procedure was performed in SigmaPlot 12.0 (Systat Software Inc.) and the functions that were used are shown in Table 5. The choice of function was based on achieving the highest R^2 - best-fit values – using as simple functions as possible.

Table 5. *Overview of the mathematical functions used to fit experimental data*.

Equation number	Curve-fit functions used in the result; SigmaPlot name	Function formula	Parameters (coefficients and constants)
13	Exponential Rise to Maximum, Double, 4 Parameter	$y = a(1 - e^{-bx}) + c(1 - e^{-dx})$	**where** *y* is hygroscopicity (or D-index) while the sum of the constants *a* and *c* refer to the maximum water uptake possible. The absorption coefficients *b* and *d* determine the rate of water uptake and *x* is time.
14	Exponential Growth, Stirling Model	$y = y_0 + \frac{a(e^{bx} - 1)}{b}$	**where** *y* is hygroscopicity (or D-index), y_0 is the amount of water gained at time 0, *a* is a constant, *b* is the water uptake coefficient and *x* is time.
15	Polynomial, Linear	$y = y_0 + ax$	**where** *y* is hygroscopicity (or D-index), y_0 is the amount of water gained at time 0, *a* is a constant describing the slope and *x* is time.
16	Exponential Rise to Maximum, Single, 2 Parameter	$y = a(1 - e^{-bx})$	**where** *y* is degree of dissolution in percent at time *x*, *a* is the maximum degree of dissolution and *b* a dissolution coefficient.
17	Exponential Growth, Single, 3 Parameter	$y = y_0 + ae^{bx}$	**where** *y* is the dissolution degree in percent, *y0* is degree of dissolution at time 0, *a* is the maximum dissolution potential and *b* a dissolution coefficient.
18	Exponential Rise to Maximum, Single, 3 Parameter	$y = y_0 + a(1 - e^{-bx})$	**where** *y* is degree of dissolution at the precipitation level *x* (mm), *y0* is the degree of dissolution at zero precipitation, *a* is the maximum dissolution potential above y0 and *b* a dissolution coefficient.

4 Results

4.1 Hygroscopicity and deliquescence of fertilisers and chemicals

4.1.1 Rates of hygroscopicity

Data on hygroscopic water uptake of the fertilisers and chemicals from moist air given in Table 2 in Appendix 1 were plotted against time shown in Figure 5. Except for Kalksalpeter™, Figure 5 and the continuous hygroscopicity results are based on four replicates although all runs are represented in the Appendix. The third replicate of Kalksalpeter™ inexplicably diverged substantially and was consequently excluded. In Figure 5, a hygroscopicity value of 2 means that 2 grams of water have been taken up by 1 gram of product. It was obvious that the pure chemicals had a much higher hygroscopicity than the fertiliser products. Furthermore, ammonium nitrate and Axan™ were more hygroscopic than the pure nitrate compound, calcium nitrate tetrahydrate. Except for Kalksalpeter™, the moisture absorption followed a double exponential function rising to maximum with four parameters (equation 13).

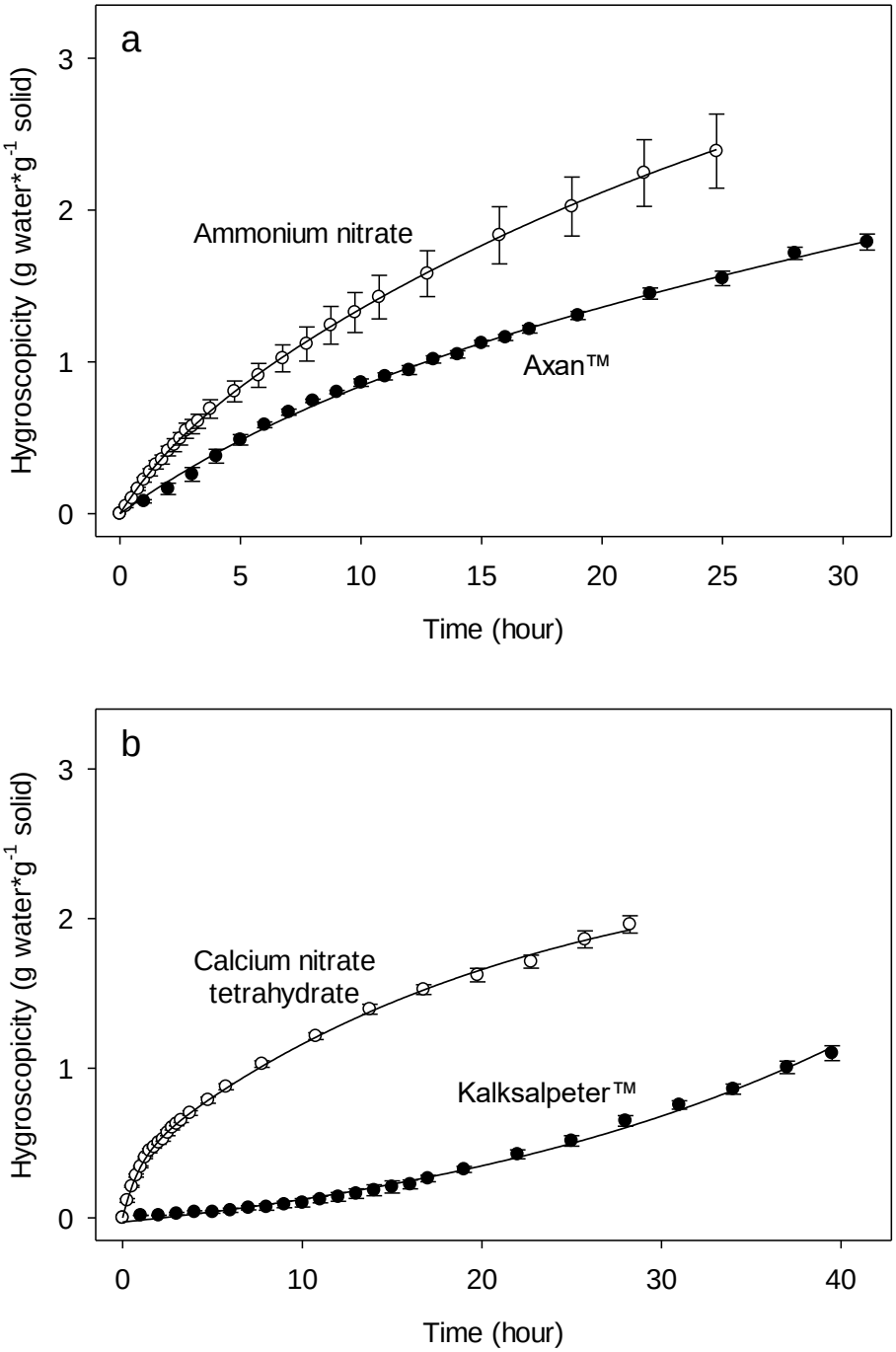

Figure 5. Hygroscopicity of (a) ammonium nitrate and Axan™ and (b) calcium nitrate tetrahydrate and Kalksalpeter™. Data is presented in grams of water absorbed per gram of compound over time. n = 4 except for Kalksalpeter™ whose third replicate was excluded (see Appendix 1).

Table 6. *Estimates of hygroscopicity parameters for fertilisers and chemicals. n = 4 except for Kalksalpeter™ (Appendix 1).*

	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™
Function used	[1]	[1]	[1]	[2]
Constants	a = 0.2922 b = 0.4335 c = 3.7555 d = 0.0333	a = 0.7614 b = 0.1036 c = 18.5264 d = 0.0019	a = 0.3579 b = 1.1389 c = 2.1163 d = 0.0477	y0 = -0.0279 a = 0.0124 b = 0.0391
R^2_{adj}	0.9998	0.9975	0.9991	0.9951

[1] $y = a(1 - e^{-bx}) + c(1 - e^{-dx})$

[2] $y = y_0 + \frac{a(e^{bx}-1)}{b}$

The absorption curve of Kalksalpeter™, on the other hand, was best fitted with a Stirling function used to describe exponential growth. Curve fitting data including adjusted R^2 values are given in Table 6. Based upon the curve-fitting results, the hygroscopicity was calculated for 2, 4, 12 and 24 hours shown in Table 7. Accordingly, calcium nitrate tetrahydrate had, after two hours, absorbed more water (0.51 g water g^{-1} solid) than any of the others, followed by ammonium nitrate (0.41). The hygroscopicity of Kalksalpeter™, on the contrary, was slow and the fertiliser did not absorb any water at all during the first hours. After 24 hours, the hygroscopicity of Axan™ was 223 % higher compared to Kalksalpeter™ (1.52 and 0.47, respectively). At that time, the ammonium nitrate had absorbed 31 % more moisture than the calcium nitrate tetrahydrate.

Table 7. *Water uptake of fertilisers and chemicals by hygroscopicity calculated from data in Table 6. n = 4 except for Kalksalpeter™ (Appendix 1).*

	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™
Time (hour)	Hygroscopicity (g water g^{-1} compound)			
2	0.41	0.21	0.51	0.00
4	0.71	0.40	0.72	0.03
12	1.53	0.96	1.28	0.16
24	2.36	1.52	1.80	0.47

Although the curve-fitting functions described the hygroscopicity well with adjusted R^2 values of 0.99 over the experimental period, the possibility to predict the hygroscopicity over a longer period than two days was limited. The maximum water uptake according to the parameters gained from the functions varied from 2.47 grams for calcium nitrate tetrahydrate to 19.29 grams for Axan™. These estimated values are, however, not realistic as the real uptake potential for all compounds, should be far higher than any of the predicted values. Thus, extrapolating data over more than two days can be misleading e.g. the never-ending exponential Stirling function which gave the best fit for Kalksalpeter™ in the measured interval but would not predict a realistic uptake outside it. Instead, it is likely that a sigmoidal function would better fit the hygroscopicity of Kalksalpeter™ if measurements had been made for a longer time.

4.1.2 Rates of dissolution

In Figure 6, the rate of dissolution (0-100%) from solid to liquid phase of fertilisers and chemicals was plotted against time.

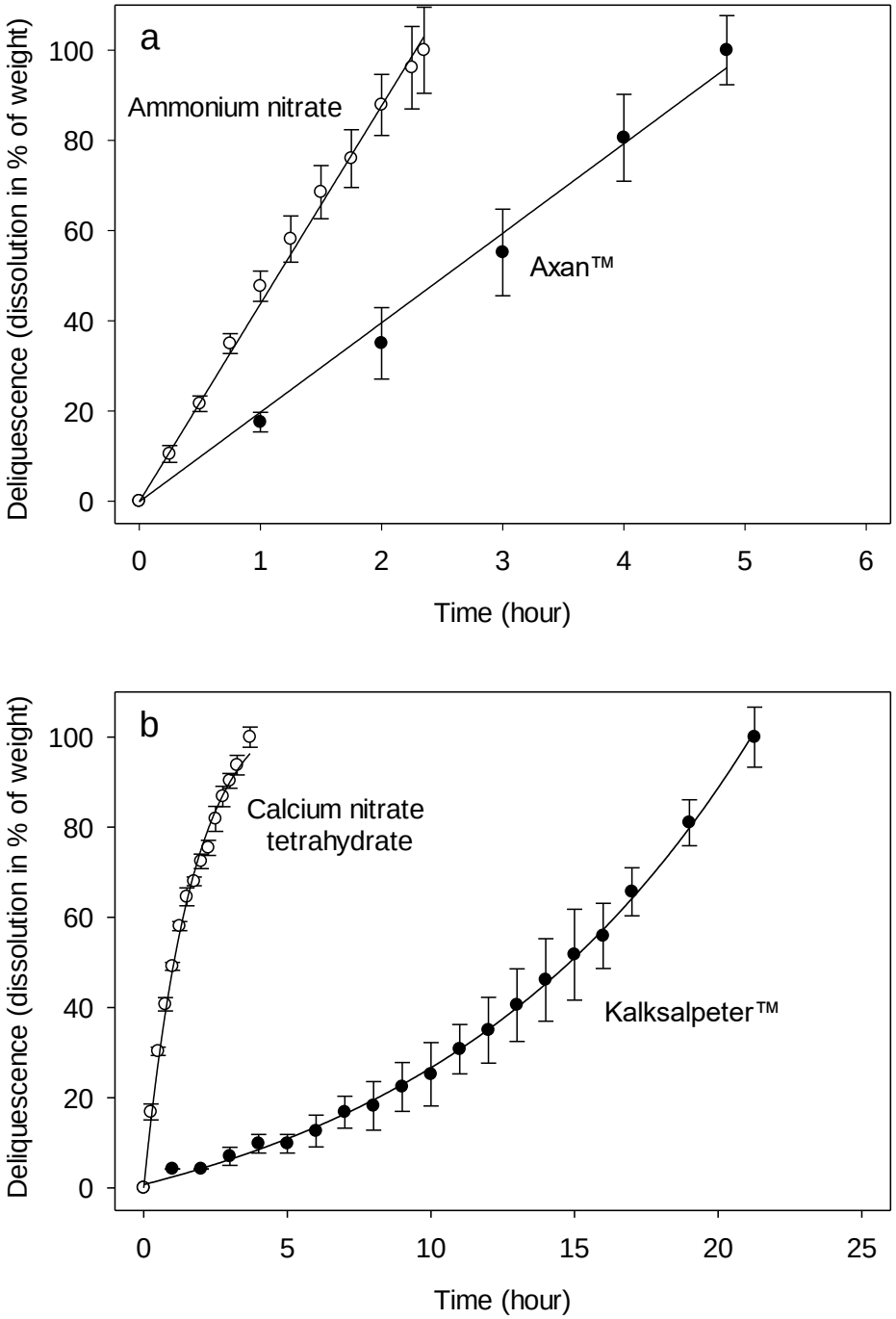

Figure 6. Dissolution from dry to liquid phase in moist air as a function of time for (a) ammonium nitrate and Axan™ and (b) calcium nitrate tetrahydrate and Kalksalpeter™. n = 4 except for Kalksalpeter™ (Appendix 1).

Table 8. *Estimates of dissolution parameters for fertilisers and chemicals during the transition from dry to liquid phase in moist air. n = 4 except for Kalksalpeter™ (Appendix 1).*

	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™
Function	[1]	[1]	[2]	[3]
Constants	y0 = 1.6990 a = 42.8392	y0 = -3.2250 a = 20.7430	a = 108.8256 b = 0.5859	y0 = -21.9028 a = 20.8388 b = 0.0609
R^2_{adj}	0.9958	0.9920	0.9941	0.9972

[1] $y = y_0 + ax$
[2] $y = a(1 - e^{-bx})$
[3] $y = y_0 + ae^{bx}$

The dissolution curves of ammonium nitrate and Axan™ were fitted with a simple linear function (equation 15) whilst calcium nitrate tetrahydrate was best fitted with a simple exponential rise to maximum function (equation 16). The dissolution data of Kalksalpeter™ followed an exponential growth function (equation 17). Estimated curve parameters are shown in Table 8.

The time needed for the compounds to reach 25, 50, 75 and 100 % dissolution, respectively, was calculated based on the parameters of Table 8 and listed in Table 9. The rate for complete dissolution was twice as high for ammonium nitrate (2.3 hours) as for the ammonium nitrate-based fertiliser Axan™ (5.0 hours). Even though pure ammonium nitrate and calcium nitrate tetrahydrate shared approximately the same hygroscopicity up to five hours, pure ammonium nitrate dissolved

Table 9. *Dissolution of fertilisers and chemicals in moist air as a function of time. Calculations are based on data presented in Table 8. n = 4 except for Kalksalpeter™ (Appendix 1).*

	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™
Degree of dissolution (%)	Time required for dissolution (h)			
25	0.5	1.4	0.4	9.6
50	1.1	2.6	1.0	14.8
75	1.7	3.8	2.0	18.4
100	2.3	5.0	4.3	21.1

much faster (Table 7). The much higher solubility of ammonium nitrate in water explains the difference. The difference in dissolution rate is even larger when comparing Axan™ with Kalksalpeter™. For Kalksalpeter to dissolve, it took almost six times longer, mainly due to their highly different hygroscopicities.

4.1.3 Deliquescence index for dissolution and dilution

Deliquescence (D) was defined as the transition from solid to liquid and described the dissolution of deliquescent solids. However, the deliquescence equation could also be used as an index (D-index) to describe the potential for dissolution and dilution of a deliquescent solid or hygroscopic solute (see 4.1.2). Thereby, the subsequent dilution following the dissolution of a deliquescent salt can be quantified. A D-index of 0.5 means a degree of dissolution of 50 %, a D-index of 1 means complete dissolution, whilst values greater than 1 show the dilution after dissolution. An index of 3 would moreover mean that the solid has dissolved completely (100 %) and thereafter been diluted two times the amount required for dissolution. In Figure 7, the index for fertilisers and chemicals was plotted against time whereupon their dissolution and dilution dynamics were presented. Hence, Figure 7 is the continuation of the dissolution graph shown in Figure 6, including values above 100 %.

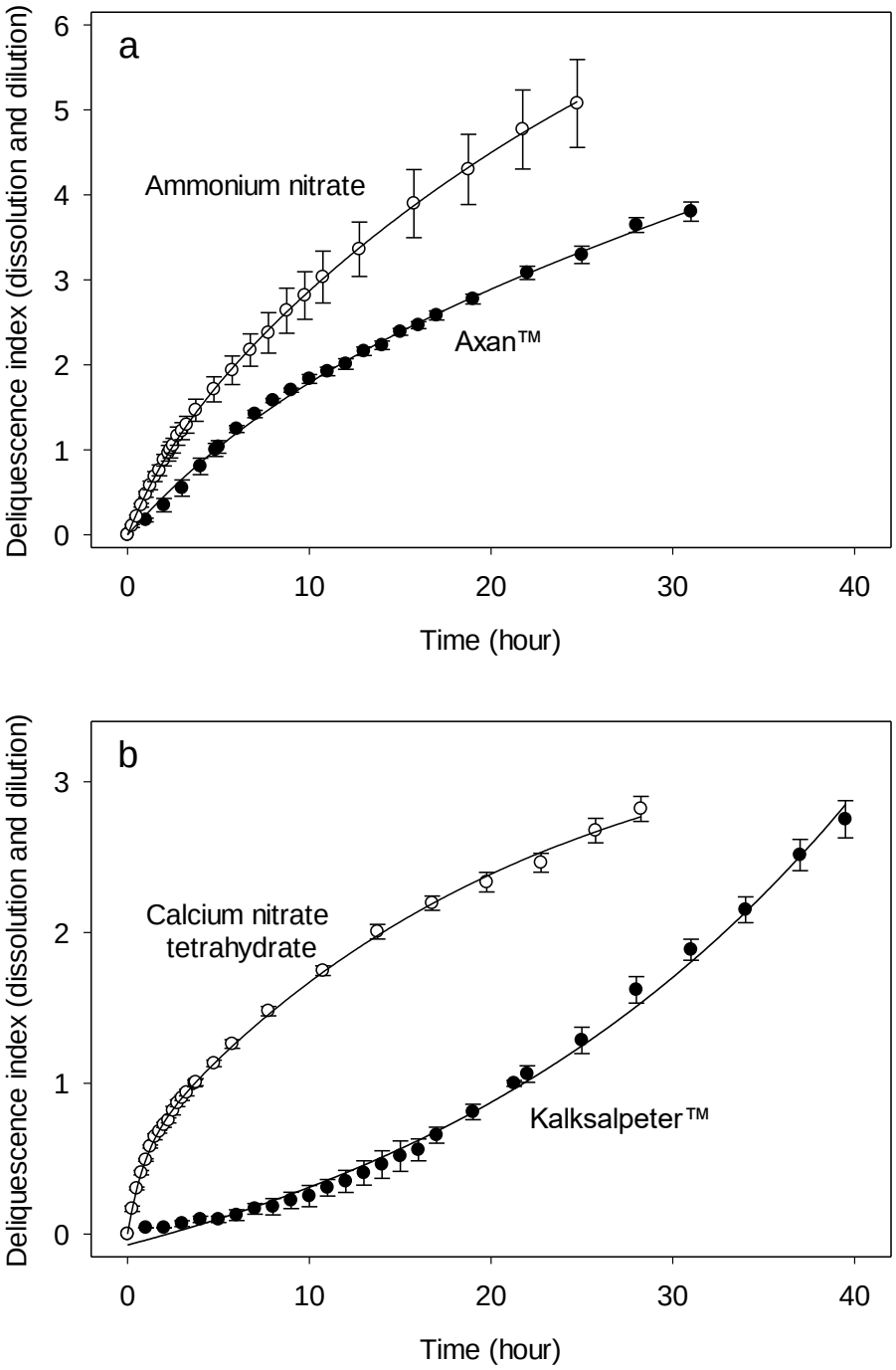

Figure 7. Deliquescence index for the dissolution and dilution potential of fertilisers and chemicals in moist air for (a) ammonium nitrate and Axan™ and (b) calcium nitrate tetrahydrate and Kalksalpeter™. An index value higher than 1 indicates dilution. n = 4 except for Kalksalpeter™ whose third replicate was excluded (Appendix 1).

Table 10. *Estimates of parameters describing water uptake of fertilisers and chemicals from moist air in relation to solubility as an index. n = 4 except for Kalksalpeter™ (Appendix 1).*

	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™
Function	[1]	[1]	[1]	[2]
Constants	a = 0.6207 b = 0.4341 c = 7.9811 d = 0.0333	a = 1.6169 b = 0.1037 c = 39.2823 d = 0.0019	a = 0.5150 b = 1.1390 c = 3.0450 d = 0.0477	y0 = -0.0433 a = 0.0183 b = 0.0383
R^2_{adj}	0.9998	0.9976	0.9991	0.9948

[1] $y = a(1 - e^{-bx}) + c(1 - e^{-dx})$

[2] $y = y_0 + \frac{a(e^{bx}-1)}{b}$

The curves in Figure 7 were fitted with the same mathematical functions used for hygroscopicity in 4.1.1 and the constants, coefficients, and R^2 values are listed in Table 10. The functions were then used to calculate index values for all compounds at 2, 4, 12 and 24 hours (Table 11).

As shown in Table 11, ammonium nitrate had the highest D-index after 24 hours (5.01) and absorbed five times the amount of water needed for its dissolution. This was twice as high as for calcium nitrate tetrahydrate (2.59) and five times higher than for Kalksalpeter™ (1.17), dissolving 117 % of its initial weight within 24 hours.

Table 11. *Index of water uptake in relation to solubility at 2, 4, 12 and 24 hours based on the parameters in Table 10. The original hygroscopicity values (Table 7) in ($g*g^{-1}$) have been bracketed. n = 4 except for Kalksalpeter™ (Appendix 1).*

	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™
Time (hour)	Index values for water uptake in relation to solubility			
2	0.87 (0.41)	0.45 (0.21)	0.74 (0.51)	0 (0)
4	1.51 (0.71)	0.85 (0.40)	1.04 (0.72)	0.06 (0.03)
12	3.25 (1.53)	2.04 (0.96)	1.84 (1.28)	0.41 (0.16)
24	5.01 (2.36)	3.23 (1.52)	2.59 (1.80)	1.17 (0.47)

Although ammonium nitrate and calcium nitrate tetrahydrate had similar hygroscopic water uptake after four hours (0.71 and 0.72, data given in brackets next to index values in Table 11), ammonium nitrate had a greater dissolution and dilution potential at that time (1.51) than calcium nitrate tetrahydrate (1.04) due to the higher solubility of ammonium nitrate.

4.1.4 Endothermic effect on vapour pressures of fertiliser solutions

Endothermic dissolution had an effect on the temperature and vapour pressure of fertilisers and salts where ammonium nitrate and Axan™ lowered the temperature and the vapour pressure of the solution the most when dissolving, followed by calcium nitrate tetrahydrate (Table 12). Kalksalpeter™ had the smallest endothermic effect. The theoretical vapour pressure of the pure water phase in each chemical solution, at the different temperatures, was also calculated whereupon the potential of decreasing the vapour pressure only by lowering the temperature was stated. Accordingly, ammonium nitrate and Axan™ lowered the vapour pressure by chilling the solution to a value far below the pressure at saturation and 25°C (8.91 and 14.94 mmHg, respectively). The enthalpy value of Kalksalpeter™ was only enough to decrease the vapour pressure to 18.60 mmHg in the pure water phase. Considering the total effect on the vapour pressures of both salt concentration and the temperature decrease during dissolution, ammonium nitrate had the lowest pressure (6.88 mmHg) which may explain its extraordinary hygroscopicity during dissolution (RH = 28.9 %).

Table 12. *Estimated change in vapour pressure of fertilisers and reference salts caused by 1) the salt concentration itself at room temperature (and saturation) and 2) the combined effect of salt concentration and change in enthalpy. In the scenario of enthalpy change, all compounds dissolved endothermically, having an additional cooling and vapour pressure lowering effect. For the enthalpy calculation, a concentration of 1 gram of solid in 5 grams of water was used to represent a saturated solution. It was assumed to lower the temperature of the solution no less than a solution at saturation.*

	Chemicals					References
	Ammonium nitrate	Axan™	Calcium nitrate tetrahydrate	Kalksalpeter™	Pure water (Reference solution)	
No change in enthalpy						
Vapour pressure (mmHg) at saturation (25°C)	14.94	[1)]14.94	12.04	Unknown	23.77	Adams & Merz, 1929; Lide, 2004
Change in enthalpy – Endothermic effect						
Enthalpy of solution ΔH (kJ mol^{-1})	+25.41	[1)] +25.41	+32.7	+88.88	-	Medvedev *et al.*, 1978;
Enthalpy of solution ΔH (kJ g^{-1})	+0.32	[1)] +0.32	+0.14	+0.08	-	Laue *et al.*, 2000; Grishchenko *et al.*, 2018
Temperature of a saturated solution (°C) when mixing salt and water (25°C)	9.7	[1)] 9.7	18.4	21	25	
Vapour pressure (mmHg) of the pure water phase at the new temperatures	8.91	[1)] 8.91	15.80	18.60	23.77	Lide, 2004
Vapour pressure (mmHg) of a saturated solution – temperature effect included	6.88	[1)] 6.88	8.88	Unknown	23.77	Adams & Merz, 1929; Lide, 2004
Corresponding relative humidity (RH) above respective solution surface (%)	28.9	28.9	37.4	-	100	

4.2 Dissolution of fertilisers by precipitation

4.2.1 Rates of dissolution

The dissolution rates of Axan™ and Kalksalpeter™ were plotted in Figure 8 in percent dissolved compound at different precipitation levels. The rates diverged where Axan™ needed less precipitation to dissolve compared to Kalksalpeter™. Both dissolution curves were best fitted with an exponential rise to maximum function (equation 18). The parameters of y0, a, b and R^2_{adj} are listed in Table 13 below.

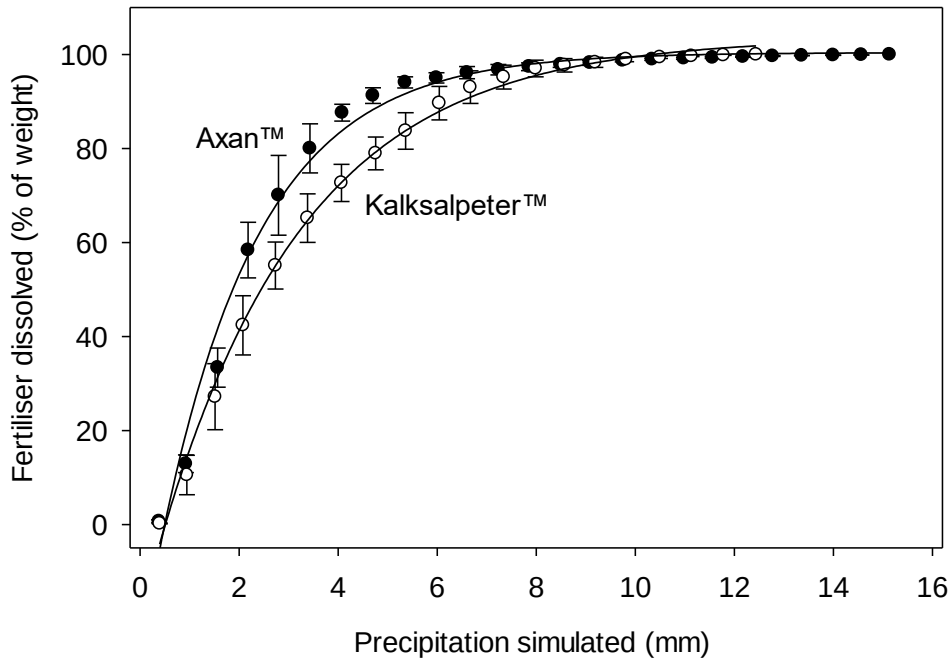

Figure 8. Dissolution of two fertilisers, Axan and Kalksalpeter as a function of water added by precipitation. n =5.

Table 13. *Estimated parameters for the dissolution of two fertilisers by simulated rainfall.*

	Axan™	Kalksalpeter™
Function	$y = y_0 + a(1 - e^{-bx})$	$y = y_0 + a(1 - e^{-bx})$
Constants	y0 = -28.5978 a = 129.0247 b = 0.5027	y0 = -19.6801 a = 123.3082 b = 0.3409
R^2_{adj}	0.9885	0.9964

Based on estimates in Table 13, the amount of precipitation required to dissolve 25, 50, 75, 90 and 100 % was calculated (Table 14). Accordingly, Kalksalpeter™ needed an additional 0.5 mm precipitation, compared to Axan™, to reach a dissolution degree of 50 %.

Considering complete dissolution (100 %), it seems, at first glance, that Kalksalpeter™ requires less water than Axan™ (10.3 versus 11.4 mm). More strikingly, the amount of precipitation needed to dissolve the very last portion of the fertilisers is disproportionately large compared to the amount during the initial dissolution. According to Table 14, Axan™ requires more precipitation for the 90-100 % dissolution (6.4 mm) than for the 0-90 % dissolution (5.0 mm). A more realistic estimate is that Kalksalpeter™ and Axan™ are completely dissolved already when reaching what is graded as 90 % dissolution degree in Table 14 and Figure 8. That corresponds to 5.0 and 6.5 mm precipitation, respectively, for Axan™ and Kalksalpeter™.

Table 14. *Precipitation (mm) needed to dissolve 25, 50, 75, 90 and 100 % of two common nitrogen fertilisers. Calculations were based on the functions presented in Table 11.*

	Precipitation (mm)	
Degree of dissolution (%)	Axan™	Kalksalpeter™
25	1.1	1.3
50	1.9	2.4
75	3.2	4.3
90	5.0	6.5
100	[1)]11.4	[1)]10.3

[1)] Values do not describe the dissolution at this point, but rather the amount of water required to remove salt residues from the net in the rain simulator.

The reason for the extended end of the dissolution curve (Figure 8) is that the 100 % dissolution degree is defined as the point where only trace levels of salt occur in the leachate water. In the rain simulation, salt residuals remained on the metal net even after dissolution whereupon the very end of the dissolution curve became misleading.

4.2.2 Dilution need of fertiliser solutions for crop uptake

The dissolution of tested fertilisers caused too high salt concentrations in solution for plant uptake. Dilution is needed and was estimated for Kalksalpeter™ and Axan™ in Table 15. Accordingly, more water was required to reach non-toxic levels for wheat than for barley due to the differences in salt tolerance between the species. A saturated solution of Kalksalpeter™ requires an additional 245.8 g of water when used in wheat compared to 144.2 g for barley. There are also differences between the fertilisers where Kalksalpeter™ needs less dilution compared to Axan™ relative its weight. However, considering the higher nitrogen content of Axan™, Kalksalpeter™ conversely needs more dilution per nitrogen unit.

Table 15. *Salinity threshold values (conductivity and salt concentration) for wheat and barley and amount of water required to reach non-toxic levels. Data for both saturated and non-saturated fertiliser solutions (corresponding to the solution after rain simulation) of Kalksalpeter™ and Axan™ are presented.*

	Kalksalpeter™		Axan™	
	Wheat	Barley	Wheat	Barley
Threshold value (dS/m)	4.7	8.0	4.7	8.0
Threshold value (g salt/ l water)	4.1	6.9	3.2	5.4
Saturated solution (1 g solid)				
Water in solution (g)	0.4	0.4	0.47	0.47
Amount of water needed to dilute to non-toxic levels (g)	245.8	144.2	312.9	183.7
Non-saturated solution (1 g solid)				
Water in solution (g)	56.3	56.3	43.3	43.3
Amount of water needed to dilute to non-toxic levels (g)	189.9	88.4	270.1	140.9

5 Discussion

5.1 Factors affecting the hygroscopicity and deliquescence of a solid

It is well accepted that the rate of hygroscopicity primarily is a function of the vapour pressure difference between a hygroscopic salt solution and the surrounding air. The salt that lowers the vapour pressure the most when dissolving in water, i.e. having a low relative humidity of hygroscopicity (RH_0), also represents the most hygroscopic compound. Comparing the pure reference chemicals with known RH_0 values at 25°C, calcium nitrate tetrahydrate with low RH_0 (50.5 %) initially was more hygroscopic than ammonium nitrate with its higher RH_0 (62.7 %) during the first two hours (Table 7). So far, the theoretic considerations and hygroscopic rates recorded in this study conform.

After four hours, the hygroscopic absorption rate of ammonium nitrate surpassed calcium nitrate tetrahydrate, indicating that other factors may have been involved. One such factor could be the size-effect as a tiny salt powder, relative its weight, has a much larger reaction surface area compared to fertiliser granules of normal size. Apart from size, factors like impurities, coating, hydration, and enthalpy appear as suggestions in the literature of agrochemicals, pharmaceuticals and other research fields where absorption of moist air is of interest. Those factors may either have

enhanced or delayed the dissolution rates and are discussed in the following sections.

5.1.1 Impurities and coating and their effects on the hygroscopicity and deliquescence of a solid

The presence of any impurity in a hygroscopic solid could increase its hygroscopicity compared to a pure reference chemical. It was emphasised by Adams & Merz (1929) that "as a rule the hygroscopicity of a mixture of two materials is greater than that of the more hygroscopic constituent", meaning that the combination of two fertiliser salts makes them more hygroscopic than if kept apart, e.g. NH_4NO_3 + $Ca(NO_3)_2$*$4H_2O$. Harris (1970) performed hygroscopic measurements on six ammonium nitrate samples, concluding that "an increase in the purity of ammonium nitrate causes a decrease in the hygroscopicity" and that "the addition of insoluble additives did not diminish the hygroscopicity of ammonium nitrate".

Hygroscopicity and deliquescence have been of great interest within the field of pharmaceutical engineering. Continuing up until recent time, further advances in the field have been made, as in the publication of Guerrieri *et al.* (2006) where the deliquescence of pharmaceuticals was thoroughly examined. They reported small levels of impurity to drastically increase the moisture sorption below RH_0, and even lower the RH_0 value itself. Moreover, Tereshchenko (2015) claimed all water sorption below RH_0 to be caused by impurities, based on the studies of adsorption and absorption processes of purified and impurified hygroscopic substances respectively. Numerous publications have also discussed the impact of crystalline and non-crystalline structure (amorphous) on the susceptibility to air moisture of pharmaceuticals. According to Newman *et al.* (2008), small amounts of amorphous structure in a crystalline solid can increase the solids propensity for air moisture. Such amorphic fractions can occur if a crystalline salt has been milled and then granulated. Presuming fertiliser salts to contain impurities of various types (Axan™ contains sulphur and magnesium), and assuming the same deliquescence mechanisms as for

pharmaceuticals and explosives (technical ammonium nitrate), fertiliser products should, based on the reasoning above, have an increased hygroscopicity and lowered deliquescent point compared to perfectly pure and crystallised reference chemicals.

It may, therefore, appear strange that the hygroscopicity of the fertilisers tested in this thesis, in neither case, was higher compared to the pure chemicals. Conversely, the hygroscopicity was 55 % higher for pure ammonium nitrate than for Axan™ and 283 % higher for calcium nitrate tetrahydrate compared to Kalksalpeter™ after 24 hours. Yet, the importance of impurities cannot be rejected as no sorption analysis or RH_0 determination was made, but the result rather shows that factors other than impurity have had a larger impact on the fertilisers' hygroscopicity. Such a factor could be the conditioning agent. As was shown by Obrestad *et al.* (1993) in a patent of Yara International, modern mineral oil based coatings may substantially reduce the hygroscopicity of ammonium nitrate and CAN by about 30-60 % (after five hours). The hygroscopicity reduction of Axan™ recorded after four hours (Table 7), as compared to the pure ammonium nitrate, was 44 %, which falls within what could be explained by the presence of the coating. Even though the coating of Kalksalpeter™ certainly lowers its sensitivity to moisture, slowing the initial hygroscopicity, it does not explain the extreme difference in hygroscopicity at four hours between calcium nitrate tetrahydrate and Kalksalpeter™ (0.72 and 0.03, respectively).

5.1.2 Water of crystallisation and hydrates affect the physicochemical properties of a hygroscopic compound

The hygroscopicity of Kalksalpeter™ diverges greatly from the other compounds tested in terms of water absorption. That is, however, not the only thing differentiating Kalksalpeter™ from Axan™, ammonium nitrate and even calcium nitrate tetrahydrate. As shown in the fertiliser specification (Table 3), Kalksalpeter™ has a molecular formula ($5Ca(NO_3)_2*NH_4NO_3*10H_2O$) different from calcium nitrate tetrahydrate ($Ca(NO_3)_2*4H_2O$). The hygroscopicity differences could, therefore, be a

function of two distinctly divergent salts. Calcium nitrate tetrahydrate and Kalksalpeter™ are hydrated by four and 10 waters of crystallisation, respectively, of which the tetrahydrate, according to the literature, should be regarded as the most hygroscopic (Hignett, 1985). An increase in hydration of a salt may reduce its melting point (as was stated for calcium nitrate), and thereby make deliquescence more likely. However, the addition of crystalline water to a deliquescent salt may, at the same time, decrease the salt's propensity to air moisture as well as decreasing its dissolution rate in water compared to its former anhydrous state (Chen, 2009). Thus, the presence of hydrates in calcium nitrate tetrahydrate and Kalksalpeter™ could eventually make them less hygroscopic compared to the anhydrous ammonium nitrate and Axan™, if the latter mechanism would be superior the melting point lowering effect.

5.1.3 Thermodynamics, enthalpy of solution, and the mechanisms affecting the hygroscopicity of a liquid

The data in Table 12 for salts and fertilisers indicate a positive correlation between hygroscopicity and enthalpy. The chemicals having the highest hygroscopicity also had the highest enthalpy of solution (ΔH) per gram of solid. Kalksalpeter™ which diverged from the others, having a low hygroscopic rate, also had a tiny endothermic effect on the vapour pressure. Unfortunately, there is no reported vapour pressure value for a saturated solution of Kalksalpeter™. However, it is likely that the highly endothermic properties of ammonium nitrate and calcium nitrate tetrahydrate have made them more hygroscopic, properties Kalksalpeter™ assuredly share, but to a significantly lesser extent. That said, the endothermic effect during dissolution could based on Table 12 and the reasoning above, initially be more important for the rate of hygroscopicity than the concentration of the salt itself. Publications discussing the effects of enthalpy on the kinetics of deliquescence are sparse. However, Van Campen *et al.* (1983) published a theoretical model aiming to describe hygroscopicity and deliquescence of pharmaceuticals in which enthalpy of dissolution was included. Nonetheless, they never included the strong endothermic properties

which may seem rare for pharmaceuticals but are more frequently occurring in the salts of common fertilisers.

The literature reviewed propose coating, impurities, structure, water of crystallisation and enthalpy to be major factors affecting the rate of hygroscopicity and deliquescence. Especially the enthalpy effect appeared to be particularly important for the vapour pressure lowering (as presented in Table 12). Nevertheless, it was not possible to quantify the individual contributions of these factors in the results as no detailed studies were performed to isolate each factor.

5.2 Dissolution by precipitation

5.2.1 Small volumes of water dissolve large amounts of fertiliser

As previously concluded, there are barely any publications or research performed on fertilisers dissolution rate by precipitation. In this thesis, the dissolution dynamics of Kalksalpeter™ and Axan™ were determined by measuring the conductivity of the drainage water. There was, however, an issue concerning small salt residuals on the metal net in the rain simulator, falsely indicating a remaining undissolved fraction of the fertiliser. The dissolution was, therefore, defined complete when 90 % of the fertiliser had dissolved and leached through the rain simulation, corresponding to 5.0 and 6.5 mm of precipitation for Axan™ and Kalksalpeter™, respectively (Figure 8). However, considering the high solubility of the two fertilisers, the solids could, theoretically, dissolve in less water.

Assuming a fertiliser granule of either type to have a diameter of 4 mm, a cross-sectional area of 12.56 mm^2 and a weight of 0.04 grams, the minimum amount of precipitation required for complete dissolution in millimetres (mm), if applied in an optimal way, can be estimated based on the respective solubility values (Figure 9). Accordingly, 1 gram of Kalksalpeter™ theoretically needs 1.27 mm of precipitation

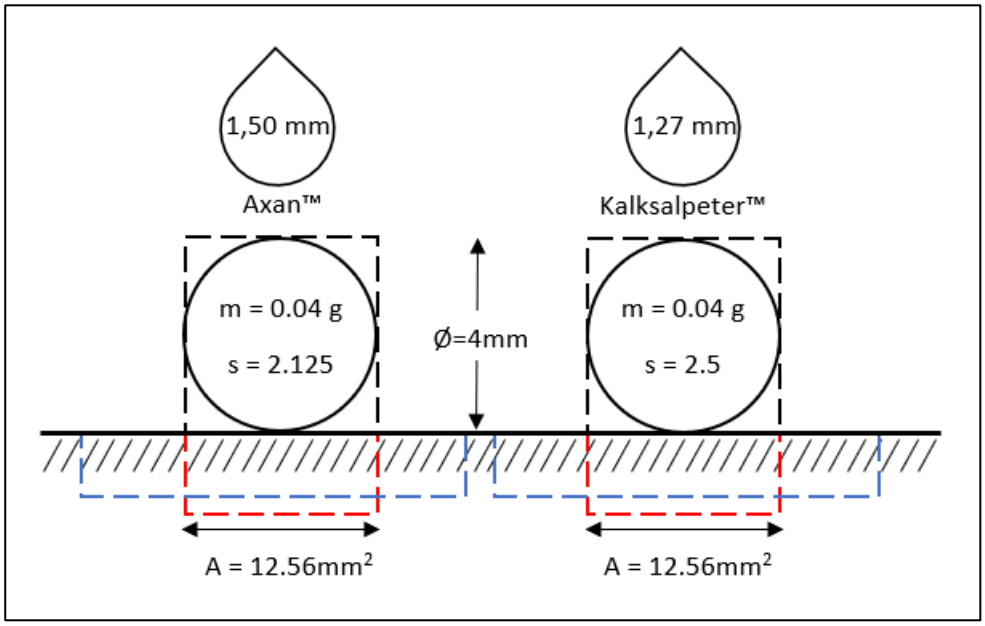

Figure 9. Theoretic estimation of the number of millimetres required to dissolve Axan™ and Kalksalpeter™ if the rain water would be applied in an optimal way, i.e. surround the solid granule until it has gone completely dissolved. Letter m refers to mass solid in grams and letter s to solubility in g solid g^{-1} water.

whilst 1 gram of Axan™ needs 1.50 mm if the rain droplets fall within the area defined in red (Figure 9). If the fertiliser granule could absorb liquid water from the surrounding soil surface (blue-marked area in Figure 9), less rain in millimetres would be required for complete dissolution.

It should be emphasised that the theoretic estimations presented in Figure 9 refer to saturated solutions whilst values measured in the simulation represent unsaturated conditions. That also explains why the measured values were higher than the calculated ones. The theoretic estimation shows the maximum dissolution potential of precipitation when water is applied in an optimal way, meaning that a proper amount of water would surround the granule and remain there during the whole dissolution phase. The dissolution was defined as completed when no additional contribution of charged ions occurred in the leachate water. In the rain simulation, more water was applied than needed as the water was sprayed at a rate exceeding that of the dissolution. The fertiliser dissolution in the field, during intense precipitation, should not be any different. The time during which the fertiliser is exposed to water

thereby seems to have a strong impact on the degree of dissolution and even small volumes of water are likely to dissolve the fertiliser if only the exposure time is sufficient.

5.2.2 High salt concentrations after dissolution limit plant uptake

Even though less precipitation than was recorded in the simulation could be enough for complete dissolution, given that moist conditions would remain over time, soil water transport and salt toxicity may still limit the fertilising effect on the plant. A highly concentrated nutrient solution, regardless if dissolved by precipitation or deliquescence, needs additional water for its dilution in order to become plant available. The dilution enables transport of dissociated free ions in the soil profile and reduces the risk of a reversed osmosis in the root-rootzone system. The dilution by rainwater is especially important if the soil profile already has a low moisture level with little or no water for the ions to diffuse in. Concerning the eventual toxic levels of a fertilising salt, plants respond adversely to salt concentrations above their tolerance level. By using the threshold values of Amacher *et al.* (2000) and data from this thesis, the need for dilution after dissolution was estimated (Table 15).

It was obvious that dissolved salts produced in the rain simulation needed dilution to become plant available. The water could be supplied either by rainfall or by available soil water. However, as precipitation alone is unlikely to supply the amounts of water needed (Table 15), soil water may be important as soils normally have high capacities for storing water. Dilution by hygroscopicity is an alternative but will take a long time as the rate of moisture absorption decreases with dilution. Yet, Table 15 is still applicable to the hygroscopicity results, as the saturated scenario also describes the dilution need after a salt formed a saturated solution by deliquescence.

5.3 Practical implications and further research

The hygroscopicity and precipitation measurements performed have shown the potential for dissolution under the given circumstances. Concerning the hygroscopicity and deliquescence of fertilisers and salts, the maximum dissolution potential and rate was determined at high relative humidities (≥90 %). However, such high humidity levels, at room temperature and combined with no precipitation, are rare why the hygroscopic rates at lower relative humidities would be of interest.

Maximum dissolution potential of fertilisers due to hygroscopicity is an important characteristic when no liquid water is available or added to the soil surface. Deliquescence by hygroscopicity is then the only possible way how solids can dissolve. However, more water is needed for further dilution in order to reach non-toxic concentrations for crops. The greatest potential of dissolving a fertiliser by hygroscopicity should, in practice, be during high air humidity together with soil moisture close to the soil surface, enabling dilution by diffusion of dissociated nutrient ions.

As was suggested in the previous discussion, the endothermic properties of the fertilisers tested may have increased their hygroscopicity. If that would be true for all endothermic salts, the enthalpy would pose an important but insufficiently discussed factor affecting the rates of hygroscopicity. By further measurements of the hygroscopicity of other common inorganic hygroscopic salts, and by including salts having either strong endothermic or exothermic properties, the impact of heat uptake or release during dissolution on hygroscopicity, could be elucidated.

The measurements showed that small volumes of water can dissolve large amounts of nitrogen fertiliser. The limitation of N availability after fertilisation in a crop production system does not seem to be the dissolution itself but rather the dilution and diffusion of dissolved ions in the soil. The concentrated fertiliser solution in the soil requires further investigation to estimate the moisture need, diffusion and dilution of ions, and time needed for the diluted ions to reach the root zone.

6 Conclusions

This thesis aimed at quantifying the dissolution dynamics of two common N fertilisers and their comparable pure salts when exposed to rainfall and air moisture, as well as identify the key mechanisms determining the rates recorded. The following conclusions were made in response to the hypotheses formulated in 1.2:

i. In a comparison of calcium nitrate tetrahydrate and ammonium nitrate, the hygroscopicity rate seemed partly correlated to their vapour pressures at saturation. Calcium nitrate tetrahydrate having a lower vapour pressure initially absorbed moisture faster than ammonium nitrate. However, other physicochemical characteristics determining the absorption rate have also been identified.
ii. Fertiliser products had lower hygroscopicity compared to their comparable pure salts. However, only ammonium nitrate and Axan™ were sufficiently comparable as calcium nitrate tetrahydrate and Kalksalpeter™, despite their various calcium nitrate contents, represent two different salts. The lower hygroscopicity of the fertilisers could be due to the presence of coating and a larger granule size.
iii. In a comparison of the two fertilisers and their reference salts, the rate of hygroscopicity seems to be affected by how endothermic the compounds are. Salts dissolving endothermically may lower the temperature and thereby the vapour pressure of the solution, increasing the hygroscopic rate.

iv. The dissolution of fertilisers by precipitation was not only a function of solubility. Kalksalpeter™ having higher solubility required more water for its dissolution than Axan™. The theoretic model in 5.2.1 showed that less water could be sufficient if water was applied optimally and with long exposure time, indicating the time factor to be important during dissolution.

In addition, the following observations were made:

v. All fertilisers and chemicals tested dissolved completely within 24 hours at high relative humidity (≥90 % at 25°C).

vi. Although hygroscopicity enables N fertilisers to dissolve in absence of rainfall, more water is needed to reach non-toxic concentrations for plant uptake and for transport to the root zone. Also the rain simulation results indicated that not the dissolution itself, but the dilution and diffusion of ions in the soil are the rate-limiting steps for crop utilisation.

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Appendix 1

Weighing of hygroscopic compounds

The mass of solid used in the hygroscopicity measurements was determined by weighing granules and powders before starting the experiment. Four replicates were used and the fertilisers and pure reference chemicals were aimed to weigh 0.60 and 0.75 g respectively. The final values received are given in Table 1 below.

Table 1. *Net weights of fertilisers and chemicals used in the hygroscopicity measurements.*

	Weight (g)			
Replicates	Axan™	Kalksalpeter™	Ammonium nitrate	Calcium nitrate tetrahydrate
1	0.59	0.60	0.68	0.69
2	0.61	0.60	0.74	0.71
3	0.60	0.60	0.74	0.75
4	0.62	0.59	0.70	0.75

Hygroscopicity, dissolution, and deliquescence index

The hygroscopicities of the compounds tested are presented in Table 2 below as mean hygroscopicity values and standard deviation. Four replicates were used in the measurements but only three Kalksalpeter™ replicates occurred in the previous result (Chapter 4). The reason was that the three replicates 1, 2 and 4 (n=3) followed each other closely and together formed a tight curve with low standard deviation, whilst replicate 3 inexplicably diverged greatly from the other giving a much higher standard deviation. As shown in Table 2, the standard deviation in the final recordings representing n=4 was 0.21 compared to 0.05 for n=3.

In the determination of dissolution rate and deliquescence index, replicate 3 for Kalksalpeter™ was again excluded. However, Table 3 shows all data received including four replicates for all compounds as a deliquescence index. For dissolution degree in percent, the dissolution index can be multiplied by 100. As for the pure hygroscopicity data, the deliquescence index shows a major difference in mean value and standard deviation depending on whether n=3 or 4. As shown in Table 3, the deliquescence index was, at time 39:30, 2.75 for n=3 and 3.05 for n=4 while the standard deviation was 0.12 and 0.53 respectively.

Table 2. *Data from hygroscopicity measurements performed at 90-99 % RH and 25°C. The mean values with standard deviation given in the table refer to the amount of water in grams absorbed per gram of solid over time (n=4). Results for Kalksalpeter™ are presented for both three and four replicates. In the results, one deviating replicate was excluded and only three replicates were presented.*

Kalksalpeter™ n=3			Kalksalpeter™ n=4			Calcium nitrate tetrahydrate			Axan™			Ammonium nitrate		
Time	Mean (g water g^{-1} solid)	Std	Time	Mean (g water g^{-1} solid)	Std	Time	Mean (g water g^{-1} solid)	Std	Time	Mean (g water g^{-1} solid)	Std	Time	Mean (g water g^{-1} solid)	Std
00:00	0.00	0.00	00:00	0.00	0.00	00:00	0.00	0.00	00:00	0.00	0.00	00:00	0.00	0.00
01:00	0.02	0.00	01:00	0.01	0.01	00:15	0.12	0.01	01:00	0.08	0.01	00:15	0.05	0.01
02:00	0.02	0.00	02:00	0.02	0.00	00:30	0.21	0.01	02:00	0.16	0.04	00:30	0.10	0.01
03:00	0.03	0.01	03:00	0.03	0.01	00:45	0.28	0.01	03:00	0.26	0.05	00:45	0.16	0.01
04:00	0.04	0.01	04:00	0.04	0.01	01:00	0.34	0.01	04:00	0.38	0.05	01:00	0.22	0.02
05:00	0.04	0.01	05:00	0.04	0.01	01:15	0.40	0.01	05:00	0.49	0.03	01:15	0.27	0.02
06:00	0.05	0.01	06:00	0.05	0.01	01:30	0.45	0.01	06:00	0.59	0.02	01:30	0.32	0.03
07:00	0.07	0.01	07:00	0.07	0.01	01:45	0.47	0.01	07:00	0.67	0.02	01:45	0.36	0.03
08:00	0.07	0.02	08:00	0.08	0.02	02:00	0.50	0.01	08:00	0.74	0.01	02:00	0.41	0.03
09:00	0.09	0.02	09:00	0.11	0.04	02:15	0.52	0.01	09:00	0.80	0.01	02:15	0.45	0.04
10:00	0.10	0.03	10:00	0.12	0.04	02:30	0.57	0.02	10:00	0.86	0.02	02:30	0.49	0.04
11:00	0.12	0.02	11:00	0.16	0.07	02:45	0.60	0.02	11:00	0.91	0.02	02:45	0.55	0.05
12:00	0.14	0.03	12:00	0.19	0.09	03:00	0.63	0.01	12:00	0.95	0.03	03:00	0.57	0.05
13:00	0.16	0.03	13:00	0.22	0.10	03:15	0.65	0.02	13:00	1.02	0.02	03:15	0.61	0.05
14:00	0.18	0.04	14:00	0.25	0.12	03:45	0.70	0.02	14:00	1.05	0.02	03:45	0.69	0.06
15:00	0.21	0.04	15:00	0.28	0.14	04:45	0.79	0.02	15:00	1.12	0.02	04:45	0.81	0.07
16:00	0.22	0.03	16:00	0.30	0.14	05:45	0.88	0.02	16:00	1.16	0.02	05:45	0.91	0.08
17:00	0.26	0.02	17:00	0.34	0.14	07:45	1.03	0.02	17:00	1.22	0.02	06:45	1.02	0.09
19:00	0.32	0.02	19:00	0.41	0.15	10:45	1.21	0.02	19:00	1.31	0.03	07:45	1.12	0.11
22:00	0.42	0.03	22:00	0.53	0.18	13:45	1.39	0.03	22:00	1.45	0.04	08:45	1.24	0.12
25:00	0.51	0.03	25:00	0.63	0.20	16:45	1.53	0.03	25:00	1.55	0.05	09:45	1.33	0.13
28:00	0.65	0.04	28:00	0.76	0.20	19:45	1.62	0.05	28:00	1.72	0.04	10:45	1.43	0.14
31:00	0.75	0.03	31:00	0.87	0.21	22:45	1.71	0.04	31:00	1.79	0.05	12:45	1.58	0.15
34:00	0.86	0.03	34:00	0.98	0.21	25:45	1.86	0.06				15:45	1.83	0.19
37:00	1.01	0.04	37:00	1.13	0.21	28:15	1.96	0.06				18:45	2.02	0.19
39:30	1.10	0.05	39:30	1.22	0.21							21:45	2.24	0.22
												24:45	2.39	0.24

Table 3. *Data from hygroscopicity measurements performed at 90-99 % RH and 25°C, presented as a deliquescence index. The dissolution degree in percent is given by multiplying index values by 100. Mean values and standard deviations are presented for each compound. Kalksalpeter™ occurs twice as four replicates were recorded but only three were presented in the result chapter. The missing values of the forth replicate are instead presented below.*

Kalksalpeter™ n=3			Kalksalpeter™ n=4			Calcium nitrate tetrahydrate			Axan™			Ammonium nitrate		
Time	D-index	Std	Time	D-index	Std	Time	D-index	Std	Time	D-index	Std	Time	D-index	Std
00:00	0.00	0.00	00:00	0.00	0.00	00:00	0.00	0.00	00:00	0.00	0.00	00:00	0.00	0.00
01:00	0.04	0.00	01:00	0.03	0.02	00:15	0.17	0.02	01:00	0.18	0.02	00:15	0.10	0.02
02:00	0.04	0.00	02:00	0.04	0.00	00:30	0.30	0.01	02:00	0.35	0.08	00:30	0.22	0.02
03:00	0.07	0.02	03:00	0.06	0.02	00:45	0.41	0.01	03:00	0.55	0.10	00:45	0.35	0.02
04:00	0.10	0.02	04:00	0.09	0.02	01:00	0.49	0.01	04:00	0.81	0.10	01:00	0.48	0.03
05:00	0.10	0.02	05:00	0.09	0.02	01:15	0.58	0.01	04:50	1.00	0.08	01:15	0.58	0.05
06:00	0.13	0.04	06:00	0.13	0.03	01:30	0.65	0.02	05:00	1.03	0.07	01:30	0.69	0.06
07:00	0.17	0.04	07:00	0.18	0.04	01:45	0.68	0.01	06:00	1.25	0.04	01:45	0.76	0.06
08:00	0.18	0.05	08:00	0.20	0.06	02:00	0.72	0.02	07:00	1.42	0.04	02:00	0.88	0.07
09:00	0.22	0.05	09:00	0.27	0.10	02:15	0.75	0.02	08:00	1.58	0.02	02:15	0.96	0.09
10:00	0.25	0.07	10:00	0.30	0.11	02:30	0.82	0.03	09:00	1.70	0.02	02:21	1.00	0.10
11:00	0.31	0.05	11:00	0.40	0.16	02:45	0.87	0.02	10:00	1.84	0.05	02:30	1.05	0.09
12:00	0.35	0.07	12:00	0.47	0.22	03:00	0.90	0.02	11:00	1.92	0.05	02:45	1.16	0.11
13:00	0.41	0.08	13:00	0.54	0.25	03:15	0.94	0.02	12:00	2.01	0.06	03:00	1.22	0.10
14:00	0.46	0.09	14:00	0.63	0.30	03:42	1.00	0.02	13:00	2.16	0.05	03:15	1.30	0.10
15:00	0.52	0.10	15:00	0.71	0.35	03:45	1.01	0.02	14:00	2.23	0.05	03:45	1.47	0.13
16:00	0.56	0.07	16:00	0.75	0.34	04:45	1.13	0.02	15:00	2.39	0.04	04:45	1.71	0.15
17:00	0.66	0.05	17:00	0.86	0.35	05:45	1.26	0.03	16:00	2.47	0.04	05:45	1.94	0.17
19:00	0.81	0.05	18:43	1.00	0.37	07:45	1.48	0.03	17:00	2.58	0.05	06:45	2.18	0.19
21:16	1.00	0.02	19:00	1.02	0.37	10:45	1.75	0.03	19:00	2.78	0.06	07:45	2.38	0.24
22:00	1.06	0.05	22:00	1.32	0.45	13:45	2.01	0.05	22:00	3.08	0.08	08:45	2.64	0.26
25:00	1.29	0.09	25:00	1.57	0.50	16:45	2.19	0.05	25:00	3.29	0.10	09:45	2.82	0.28
28:00	1.62	0.09	28:00	1.90	0.49	19:45	2.33	0.06	28:00	3.65	0.09	10:45	3.03	0.30
31:00	1.89	0.07	31:00	2.18	0.52	22:45	2.46	0.06	31:00	3.80	0.11	12:45	3.36	0.32
34:00	2.15	0.09	34:00	2.46	0.54	25:45	2.68	0.08				15:45	3.90	0.40
37:00	2.51	0.10	37:00	2.81	0.52	28:15	2.82	0.08				18:45	4.30	0.41
39:30	2.75	0.12	39:30	3.05	0.53							21:45	4.77	0.47
												24:45	5.08	0.52

Appendix 2

Conversion factor between concentration and conductivity

For converting the conductivity values recorded during the rain simulation into concentrations, a conversion factor was introduced. By preparing four solutions of each fertiliser in four different concentrations and measuring their respective conductivities, a conversion factor (k) was found by using a simple linear function y=kx+m. In Table 4, the relationship between concentration in ppm (calculation based upon an exact weighing of respective chemical) and conductivity in µS/cm (measured in the lab) is shown together with respective equation, including the conversion factor (k-values).

Table 4. *The relation between salt concentration (ppm) and its conductivity (µS/cm) for Axan™ and Kalksalpeter™. Four different concentrations and four replicates were prepared and the exact concentrations (ppm) and their respective conductivity were tabulated. The equation presented for each replicate and as a mean expresses the conversion factor (k) in y=kx+m. The conversion factor can be used for converting measured conductivities into concentrations.*

Concentration	Replicates (Axan™)								Replicates (Kalksalpeter™)							
	1		2		3		4		1		2		3		4	
(g salt*kg^{-1} water)	ppm	cond	ppm	cond	ppm	cond	ppm	cond	ppm	cond	ppm	cond	ppm	cond	ppm	cond
0	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
0.5	499	804	508	802	509	812	508	804	499	623	499	613	489	599	499	608
1	999	1551	1017	1555	1019	1561	1017	1569	998	1209	998	1185	979	1159	998	1180
2	1940	2870	1975	2890	1973	2930	1976	2940	1986	2300	1985	2300	1946	2270	1974	2300
Equation	y = 1.4728x + 40.788		y = 1.4574x + 36.589		y = 1.4784x + 32.27		y = 1.4833x + 30.304		y = 1.1529x + 29.236		y = 1.1541x + 20.208		y = 1.1618x + 15.527		y = 1.1609x + 14.602	
Mean	y = 1.473x + 34.987								y = 1.1574x + 19.89							

Appendix 3

Dissolution by precipitation

In the rain simulation, about 0.6 grams of each fertiliser was dissolved and five replicates were used. The detailed number of granules and the exact weight of respective fertiliser in each run are presented in Table 5. The dissolution degree as a function of precipitation, calculated from the dissolution data, is presented in Table 6.

Table 5. *Number and weight of fertiliser granules used in the rain simulation.*

	Axan™		Kalksalpeter™	
Replicates	Number of granules	Weight (g)	Number of granules	Weight (g)
1	16	0.61	22	0.60
2	16	0.62	23	0.61
3	17	0.61	23	0.61
4	18	0.61	22	0.61
5	19	0.60	25	0.60

Table 6. *Dissolution of fertilisers (%) at various cumulative precipitation levels (mm).*

Axan™			Kalksalpeter™		
Cumulative precipitation (mm)	Mean dissolution (%)	Standard deviation	Cumulative precipitation (mm)	Mean dissolution (%)	Standard deviation
0.0	0.0	0.0	0.0	0.0	0.0
0.4	0.7	0.3	0.4	0.2	0.1
0.9	12.9	1.9	0.9	10.5	4.2
1.6	33.4	4.2	1.5	27.2	7.0
2.2	58.4	5.9	2.1	42.4	6.3
2.8	70.1	8.5	2.7	55.1	5.0
3.4	80.0	5.2	3.4	65.2	5.2
4.1	87.6	1.8	4.1	72.7	4.0
4.7	91.3	1.7	4.8	79.0	3.5
5.4	94.1	1.2	5.4	83.8	3.9
6.0	95.1	1.1	6.0	89.7	3.6
6.6	96.2	1.3	6.7	93.1	3.5
7.2	96.8	1.1	7.3	95.2	2.5
7.8	97.4	0.8	8.0	97.1	1.8
8.5	97.9	0.6	8.6	97.7	1.4
9.1	98.3	0.5	9.2	98.3	1.1
9.7	98.8	0.3	9.8	99.0	0.5
10.3	99.0	0.2	10.5	99.4	0.3
11.0	99.2	0.2	11.1	99.7	0.1
11.6	99.4	0.2	11.8	99.9	0.0
12.2	99.5	0.1	12.4	100.0	0.0
12.8	99.7	0.1			
13.4	99.8	0.0			
14.0	99.9	0.0			
14.6	99.9	0.0			
15.1	100.0	0.0			